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In re Japanese Application of

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for: "Method of Vapor Phase Growth of Metal Oxide Dielectric Film"

VERIFICATION OF TRANSLATION

Honorable Commissioner of Patents and Trademarks

Washington, D.C. 20231

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Katsuhiro ITO

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[Title of the Invention] METHOD OF VAPOR PHASE GROWTH  
OF METAL OXIDE DIELECTRIC FILM

[Claims]

[Claim 1] A vapor phase growth method of a metal oxide dielectric film on a substrate using organometal gases, comprising: a step of carrying out film formation by introducing the organometal gases and an oxidizing gas into a vacuum chamber through separate introduction inlets while heating the substrate set in the vacuum chamber and keeping the total pressure of the vacuum chamber at  $1 \times 10^{-2}$  Torr or lower.

[Claim 2] A vapor phase growth method of a metal oxide dielectric film according to claim 1, wherein the substrate temperature is at 450°C or lower during the film formation.

[Claim 3] A vapor phase growth method of a metal oxide dielectric film according to claim 1 or 2, wherein the total pressure of the vacuum chamber is at  $1 \times 10^{-4}$  Torr or higher and  $1 \times 10^{-2}$  Torr or lower.

[Claim 4] A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 3, wherein the oxidizing gas comprises nitrogen dioxide gas.

[Claim 5] A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 4, wherein the film formation is carried out by

controlling the gas supply conditions for the organometal gases and/or the oxidizing gas to be self-controlling gas supply conditions as to obtain the metal oxide dielectric film having a prescribed composition and crystal structure.

[Claim 6] A vapor phase growth method of a metal oxide dielectric film according to the claim 5, wherein the flow rates of organometal gases and the oxidizing gas are directly controlled without using a carrier gas to introduce the organometal gases and the oxidizing gas into the vacuum chamber.

[Claim 7] A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 6, wherein the metal oxide dielectric film is a PZT film or a BST film.

[Claim 8] A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 7, wherein the substrate has capacitor electrodes formed thereon which comprises at least any one of metals or metal oxides of Pt, Ir, Ru, IrO<sub>2</sub>, RuO<sub>2</sub>, TiN, or WN and the metal oxide dielectric film is formed on the substrate in vapor phase.

[Claim 9] A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 8, wherein the substrate has an Al wiring formed thereon and the metal oxide dielectric film is formed on the substrate in vapor phase.

[Claim 10] A vapor phase growth method of a metal oxide dielectric film according to any one of claims 1 to 9, wherein the temperature of the inner walls of the vacuum chamber is equal to or higher than a temperature to allow the organometal gases to have a sufficiently high vapor pressure and equal to or lower than an organometal gas decomposition temperature.

[Claim 11] A method for fabricating a semiconductor device, comprising: a step of forming a MOS-type transistor on a semiconductor substrate, a step of forming a first interlayer insulation film on the transistor, a step of forming electric conduction by opening a contact reaching the diffusion layer of the MOS-type transistor in the first interlayer insulation film and burying a metal plug in the contact, a step of forming a capacitor lower part electrode layer on the whole surface of the first interlayer insulation film having the metal plug, a step of forming a metal oxide dielectric film on the whole surface of the capacitor lower part electrode layer using organometal gases and an oxidizing gas at  $1 \times 10^{-4}$  Torr or higher to  $1 \times 10^{-2}$  Torr or lower of the total pressure while keeping the temperature of the semiconductor substrate at 450°C or lower, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the lower part electrode layer, the metal oxide dielectric film, and the capacitor

upper part electrode layer to obtain a capacitor with a three-layered laminated structure.

[Claim 12] A method for fabricating a semiconductor device, comprising: a step of forming a MOS-type transistor on a semiconductor substrate, a step of forming a first interlayer insulation film on the transistor, a step of forming electric conduction by opening a contact reaching the diffusion layer of the MOS-type transistor in the first interlayer insulation film and burying a metal plug in the contact, a step of forming a capacitor lower part electrode layer on the whole surface of the first interlayer insulation film having the metal plug, a step of forming a capacitor lower part electrode on the metal plug by patterning the capacitor lower part electrode, a step of forming a metal oxide dielectric film on the patterned capacitor lower part electrode and on the whole surface of the first interlayer insulation film using organometal gases and an oxidizing gas at  $1 \times 10^{-4}$  Torr or higher to  $1 \times 10^{-2}$  Torr or lower of the total pressure while keeping the temperature of the semiconductor substrate at  $450^{\circ}\text{C}$  or lower, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the capacitor upper part electrode layer to obtain a capacitor with a three-layered laminated structure of the capacitor lower part electrode, the metal oxide dielectric film, and the capacitor upper

part electrode.

[Claim 13] A method for fabricating a semiconductor device, comprising: a step of forming a MOS-type transistor on a semiconductor substrate, a step of forming a first interlayer insulation film on the transistor, a step of forming electric conduction by opening a contact reaching the diffusion layer of the MOS-type transistor in the first interlayer insulation film and burying a metal plug in the contact, a step of forming an aluminum wiring electrically connected to the metal plug on the first interlayer insulation film, a step of forming a second interlayer insulation film on the aluminum wiring, a step of forming electric conduction by opening a contact reaching the aluminum wiring in the second interlayer insulation film and burying a metal plug, a step of forming a capacitor lower part electrode layer on the whole surface of the second interlayer insulation film including the metal plug, a step of forming a metal oxide dielectric film on the whole surface of the capacitor lower part electrode layer using organometal gases and an oxidizing gas at  $1 \times 10^{-4}$  Torr or higher to  $1 \times 10^{-2}$  Torr or lower of the total pressure while keeping the temperature of the semiconductor substrate at  $450^{\circ}\text{C}$  or lower, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the capacitor lower part electrode



layer, the metal oxide dielectric film, and the capacitor upper part electrode layer to obtain a capacitor with a three-layered laminated structure.

[Claim 14] A method for fabricating a semiconductor device according to claim 13, wherein aluminum wiring to be formed in the lower layer of the capacitor is made multilayered by repeating, at least one time before the capacitor lower part electrode layer is formed, a step of forming an aluminum wiring electrically conducting to the finally formed metal plug, a step of forming an interlayer insulation film on the aluminum wiring, and a step of forming electric conduction by opening a contact reaching the aluminum wiring in the interlayer insulation film and burying a metal plug in the contact.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a fabrication method of a semiconductor device having capacitor elements, more specifically, the present invention relates to a fabrication method of a high-dielectric-constant film and a ferroelectric film to be used for a capacitor and a gate of a semiconductor integrated circuit using raw materials of organometal gases.

[0002]

[Prior Art]

In recent years, ferroelectric memories using

ferroelectric capacitors, dynamic random access memories (DRAMs) using high-dielectric-constant capacitors, and the likes have actively been investigated and developed. These ferroelectric memories and DRAMs comprise selective transistors and store information using capacitors, as memory cells, connected to one diffusion layer of each selective transistor. The ferroelectric capacitors are provided with, as a capacitive insulating film, a ferroelectric film such as  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (hereafter referred to as PZT) or the like and enabled to store non-volatile information by polarizing the ferroelectric film. Meanwhile, the high-dielectric-constant capacitors are provided with, as a capacitive insulating film, a high-dielectric-constant thin film of  $(\text{Ba}, \text{Sr})\text{TiO}_3$  (hereafter referred to as BST), so that the capacitors have high capacitance and enable elements to be miniaturized in a fine structure.

[0003]

In the case of using such ceramic materials for semiconductor elements, it is highly important to deposit such ceramic materials in a thin film with excellent crystallinity on a conductive film to be a lower electrode. As the method for depositing a thin film, there have conventionally been reported a sol-gel method, a sputtering method, and a CVD method.

[0004]

The sol-gel method is a method in which organometal

materials dissolved in an organic solvent are applied to a wafer having a lower electrode formed thereon, by a spin coating, and crystallized by annealing in oxygen. In the method, since crystallization takes place in a solid phase, the temperature for the crystallization is necessary to be very high and in the case of using PZT for a metal oxide dielectric film, the crystallization temperature required to acquire sufficient ferroelectric properties is 600°C and in the case of BST, the crystallization temperature required to acquire sufficiently high dielectric properties is 650°C. A crystal formed by the foregoing method has a defect that the orientation of the crystal is uneven. Further, the sol-gel method is difficult to be applied to a wafer with a large diameter and furthermore, the method is inferior in coating of stepped surfaces and thus unsuitable for high integration of a device.

[0005]

The sputtering method is a method in which a film is formed on a wafer having electrodes thereon, by reactive sputtering of a ceramic sintered body to be formed into the film using Ar + O<sub>2</sub> plasma and then subjected to crystallization by annealing in oxygen. The film can be made even by making the diameter of the target wide and a sufficiently high film formation speed can be obtained by increasing the power for plasma generation. However, in the sputtering method as well,

the crystallization is required to be carried out at a high temperature and in the case of using PZT for a metal oxide dielectric film, the crystallization temperature required to acquire sufficient ferroelectric properties is 600°C and in the case of BST, the crystallization temperature required to acquire sufficiently high dielectric properties is 650°C. Further, in the sputtering method, since the composition of the film obtained is substantially determined by the composition of the target used, the target has to be replaced in order to change the composition and that is disadvantageous from a viewpoint of production process.

[0006]

The CVD method is a method in which raw materials are transferred in gaseous state to a vacuum chamber to form a film. It is considered that the CVD method is excellent in uniform film formation on a wafer with a large diameter and in coating property on stepped surfaces and highly expected as a technique for mass production in the case of application to ULSI. The metals of constituent elements of a metal oxide dielectric film are Ba, Sr, Bi, Pb, Ti, Zr, Ta, La, and the likes and since proper hydrides and chlorides of these metals are very few, organometals are used for vapor phase growth. However, these organometals have low vapor pressures and are mostly solids or liquid at a room temperature and, therefore, a transferring method using a

carrier gas is employed.

[0007]

Fig. 2 is a diagrammatic illustration illustrating the reaction gas supply method in the case of using a carrier gas. The apparatus is composed of a thermostatic tank 201, a bottle 202, organometal raw materials 203 made ready in the bottle, a supply pipe 204 for an inert carrier gas such as Ar, N<sub>2</sub>, and the likes, a mass flow controller 210 for the carrier gas, a supply pipe 205 for organometal gases to be transferred by the carrier gas, a growth chamber 207 equipped with a heating mechanism 206, a gas discharge port 209, and so forth.

[0008]

The organometal materials 203 made ready in the bottle are, for example, strontium bis(dipivaloylmethanate) {abbr. Sr(DPM)<sub>2</sub>}, barium bis(dipivaloylmethanate) {abbr. Ba(DPM)<sub>2</sub>}, and lead bis(dipivaloylmethanate) {abbr. Pb(DPM)<sub>2</sub>}, and maintain solid or liquid state at a normal temperature. In the CVD method using the apparatus, these organometal materials are sublimated in the bottle 202 and supplied to the growth chamber 207 while being accompanied with a carrier gas supplied from the supply pipe 204 to form a film on a heated wafer 208. The pressure during the film formation at that time is the atmospheric pressure or a pressure of several Torr.

[0009]

In the case such a method is employed, however, there is a disadvantageous point that the organometal gas flow rates in the carrier gas are difficult to be quantified and precisely controlled. That is because the carrier gas contains organometal gases in an amount equal to or more than the amount corresponding to the saturated vapor pressure determined by the temperature of the thermostatic tank 202 and because the flow rates of the organometal gases depend not only on the flow rate of the carrier gas but also on the surface area of raw material solids and the temperature of the thermostatic tank. According to the description of Jpn. J. Appl. Phys. Vol. 32 (1993) P. 4175 on the formation of a film of PTO (lead titanate:  $\text{PbTiO}_3$ ) by the above film formation method, the temperature of the formation of a PTO film is very high, as high as  $570^\circ\text{C}$ , and the film obtained has a drawback point that crystal orientation is uneven.

[0010]

Description regarding a method for forming a thin film by supplying reactive molecules to a substrate in a decreased pressure is given in Japanese Patent Laid-Open No. 5-251355. The film formation method described in the publication of the patent aims to improve the gas utilization efficiency and the evenness of the film thickness and describes a thin film formation method using a gas in which the pressure of the inside of a vacuum chamber is set so as to make the average free

movement path of molecules contained in the supplied reactive gas longer than the shortest distance between a substrate the vacuum chamber and the exposed wall in the vacuum side of the vacuum chamber. This publication of the patent describes the correlation of the average free movement path  $d$  (m) of molecules to the temperature (K) of the gas, the pressure  $P$  (Pa) of the gas and the diameter  $D$  (m) of the gas molecule. As being defined as  $d = 3.11 \times 10^{-24} \times T / (P \times D^2)$ , the average free movement path is in inverse proportion to the second power of the diameter of the molecule of the gas. Since the diameter of the molecule of an organometal gas is 10 times as large as the diameter of  $\text{Si}_2\text{H}_6$  molecule described in the publication of the patent, the average free movement path of the organometal gas is 1/100 of the average free movement path of  $\text{Si}_2\text{H}_6$  or shorter. Subsequently, by the method described in the publication of Japanese Patent Laid-Open No. 5 - 251355, in terms of the apparatus, if a distance applicable for production is kept between a substrate and the vacuum side exposed wall of a vacuum chamber, the pressure of the vacuum chamber has to be set at  $1 \times 10^{-5}$  Torr.

[0011]

In the case of forming a metal oxide dielectric film, it is required to introduce an oxidizing gas to sufficiently oxidize a metal supplied in a form of an organometal. In the atmosphere as thin as  $1 \times 10^{-5}$  Torr

or thinner, it occurs a problem that oxidization cannot sufficiently be carried out, which causes deterioration of crystallinity. Further, in the atmosphere as thin as  $1 \times 10^{-5}$  Torr or thinner, it occurs a problem that the supply amount of a raw material to the substrate surface is a little and the film formation ratio is slow and that the cost is too high in the case of employing such a method for a semiconductor device fabrication method. Consequently, though the method is efficient for a molecule with a small diameter such as  $\text{Si}_2\text{H}_6$ , it is difficult to apply the method for film formation of a metal oxide dielectric film where a large molecule is used and sufficient oxidation is required. Furthermore, the substrate temperature described is very high, as high as about  $700^\circ\text{C}$ , so that the method is not suitable for the purpose of the present invention required to carry out film formation at a relatively low temperature. Moreover, no description is given regarding the orientation of the film, which is a very important and required property for a metal oxide dielectric film.

[0012]

In conventional production of a ferroelectric memory or a DRAM, the foregoing film formation methods are employed, however heating at a high temperature around  $600^\circ\text{C}$  or higher in oxygen atmosphere is essential and crystal orientation has been difficult to be controlled.



[0013]

To give a description of a semiconductor in terms of the structure, in order to make a ferroelectric capacitor and a high-dielectric-constant capacitor well functioning, it is required to electrically connect an electrode of either one of capacitors to a diffusion layer of a selective transistor. Conventionally, in a DRAM, it is general that polysilicon connected to one diffusion layer of a selective transistor is used as one electrode and that a  $\text{SiO}_2$  film, a  $\text{Si}_3\text{N}_4$  film, or the like is formed as a capacitive insulating film on the surface of the polysilicon to compose the capacitor structure. However, since the ceramic thin film is an oxide, polysilicon is oxidized when the thin film is to be formed directly on the surface of the polysilicon and owing to that, it is impossible to form a good thin film. Hence, 1995 Symposium on VLSI Technology Digest of Technical Papers p. 123 describes a cell structure in which the upper electrode of a capacitor and a diffusion layer are connected by a local wiring of a metal such as Al or the like. Also, International Electron Devices Meeting Technical Digest, 1994 p. 843, describes a technique of forming a PZT capacitor on polysilicon using a TiN barrier metal. Regarding a DRAM, for example, International Electron Devices Meeting Technical Digest, 1994 p. 831, describes a technique of forming a STO (strontium titanate  $\text{SrTiO}_3$ ) thin film on a  $\text{RuO}_2/\text{TiN}$  lower

electrode form on a polysilicon plug to compose a capacitor.

[0014]

[Problem to be Solved by the Invention]

However, the following problems exist in the foregoing film formation methods. A first problem is that since the crystallization temperature of the metal oxide dielectric film is as high as 600°C or higher, even if TiN is used as a barrier metal as described International Electron Devices Meeting Technical Digest p. 843, oxidation of TiN is inevitable and the contact resistance is increased. Further, it is also difficult to use W and Al for a material of a plug instead of polysilicon. That is because W is easy to be oxidized and the temperature exceeds the melting point of Al. The practical upper limit temperatures of the respective metals are around 500°C for TiN and around 450°C for W, Al.

[0015]

In Jpn. J. Appl. Phys. vol. 32 (1993) p. 4057, a sputtering method described is a method for controlling a composition and lowering the crystallization temperature of PZT to 415°C by simultaneously sputtering multiple targets of respective constituent metal oxides. However, the sputtering method has problems that the method is inferior in coating on stepped surfaces and that the method is difficult to be applied for film formation on

side wall parts of a stack type or a trench type capacitor, and therefore, the method cannot be a countermeasure to a capacitor production technique for a semiconductor integrated circuit.

[0016]

A second problem is that the properties of a dielectric film are deteriorated in the case of making the film thin. In order to achieve a high speed and make the structure ultrafine, it is essential to lower the voltage of a power source and in order to provide an electric field necessary for a capacitive insulating film, it is necessary to make the capacitive insulating film of the metal oxide dielectric film as thin as possible. Fig. 3 illustrates the film thickness and spontaneous polarization  $2P_r$  in the case of forming a PZT film on Pt by a sol-gel method. In the case of 200 nm or thinner of the film thickness, the spontaneous polarization value is found sharply decreased. A similar phenomenon is also observed in the case of BST. There exists a problem that the dielectric constant of a BST film formed on  $\text{RuO}_2$  by a CVD method is sharply decreased in the case of 50 nm or thinner of the film thickness. That is attributed to inferior crystallinity in the vicinity of the interface of a lower part electrode. Owing to the foregoing problems, conventional film formation methods are found difficult to make a capacitive insulating film thin and to lower the voltage of a power source.

[0017]

A third problem is that the orientation of the film cannot be controlled. To make the orientation even is advantageous in the following points. At first, the grain boundaries of the polycrystal become continuous to lower the current leakage. Secondary, the dielectric constant can be increased and the spontaneous polarization can be heightened by conforming the polarization direction to the electric field direction.

[0018]

According to the description in Jpn. J. Appl. Phys. Vol. 32 (1993) P. 4075, it is described that PZT is epitaxially grown on a single crystal substrate of MgO(100) or Pt(100)/MgO(100) by a sputtering method and PZT significantly tends to be oriented to (001) orientation. However, it is also described that orientation is uneven in the case where a film is formed on polycrystalline Pt oriented to (111) just like for the case of Pt(111)/Ti/SiO<sub>2</sub> and considering that the capacitor electrodes of a semiconductor integrated circuit are polycrystalline, such a method cannot be a countermeasure.

[0019]

A fourth problem is a problem of dust adsorption during film formation. In any conventional film formation method, e.g. a sol-gel method, a sputtering method, and a CVD method, with the film growing, raw

materials or products adhere to an apparatus inner wall part or to a susceptor part or the like holding a wafer. Subsequently, adhered raw materials or products are parted and peeled off, then, these materials adhere to the wafer surface to cause a problem that device fabrication thereafter is obstructed.

For example, in a sol-gel method, a raw material solution is scattered to the apparatus inner walls at the time of spin coating and segments of a film of the dried scattered raw material adhere to the wafer surface. Also in a sputtering method, a material of a target adheres to the apparatus inner walls and being parted and scattered, the material pollutes the wafer surface.

In terms of a CVD method, in the case of a kind of methods employing a furnace for heating a wafer put therein by increasing the temperature of the walls, organometal gases are decomposed in the heated walls and the decomposed matter is scattered and pollutes the wafer surface.

[0020]

As described above, there are a lot of problems to be solved in formation of a thin film capacitor of a metal oxide dielectric material on a plug and in formation of a metal oxide dielectric thin film capacitor on a multilayer metal wiring structure and thus the cell surface area cannot easily be narrowed just like a conventional DRAM and a flash memory and consequently,

the integration degree has still been low.

[0021]

The present invention is developed while taking the above described problems in conventional methods for forming a capacitive insulation film of a metal oxide dielectric film into consideration and aims at providing a vapor phase growth method of a metal oxide dielectric film and capable of forming a metal oxide with excellent in both orientation and crystallinity on a plug at a low temperature and further aims at providing a semiconductor device made to have a fine structure, highly integrated, and multilayered and metallized by employing the vapor phase growth method.

[0022]

[Means for Solving the Problem]

The present invention relates to a vapor phase growth method of a metal oxide dielectric film on a substrate using organometal gases, that is, a vapor phase growth method of a metal oxide dielectric film, comprising a step of: introducing organometal gases and an oxidizing gas into a vacuum chamber through separate introduction inlets while heating the substrate set in the vacuum chamber and keeping the total pressure in the vacuum chamber at  $1 \times 10^{-2}$  Torr or lower.

[0023]

The vapor phase growth of film on a substrate is carried out preferably keeping the substrate temperature

at 450°C or lower during the film formation and keeping the total pressure of the vacuum chamber at  $1 \times 10^{-4}$  Torr or higher in order to obtain a practically high film formation rate.

[0024]

Further, in an embodiment of the present invention, the foregoing oxidizing gas characteristically comprises nitrogen dioxide.

[0025]

Furthermore, in another embodiment of the present invention, the film formation is carried out while controlling the gas supply conditions for the foregoing organometal gas and/or the foregoing oxidizing gas to be self-controlling conditions to obtain the foregoing metal oxide dielectric film having a prescribed composition and a crystal structure.

[0026]

Moreover, in this vapor phase growth method, it is preferable to directly control the flow rates of the foregoing organometal gas and oxidizing gas without using a carrier gas and to introduce them to the foregoing vacuum chamber.

[0027]

Further, in an embodiment of the invention, the foregoing metal oxide dielectric film may be a PZT film or a BST film.

[0028]

In addition to that, a substrate having at least capacitor electrodes comprising a metal or a metal oxide of Pt, Ir, Ru, IrO<sub>2</sub>, RuO<sub>2</sub>, TiN, or WN thereon may be employed as the substrate.

[0029]

In an embodiment of the present invention, the substrate has an electric wiring made of Al.

[0030]

Furthermore, in the foregoing vapor phase growth method, the temperature of the inner walls of the vacuum chamber may be equal to or higher than a temperature to allow the organometal gases to have a sufficiently high vapor pressure and equal to or lower than an organometal gas decomposition temperature.

[0031]

The present invention further relates to a method for fabricating a semiconductor device, comprising: a step of forming a MOS-type transistor on a semiconductor substrate, a step of forming a first interlayer insulation film on the transistor, a step of forming electric conduction by opening a contact reaching the diffusion layer of the MOS-type transistor in the first interlayer insulation film and burying a metal plug in the contact, a step of forming a capacitor lower part electrode layer on the whole surface of the first interlayer insulation film having the metal plug, a step of forming a metal oxide dielectric film on the whole



surface of the capacitor lower part electrode layer using organometal gases and an oxidizing gas at  $1 \times 10^{-4}$  Torr or higher to  $1 \times 10^{-2}$  Torr or lower of the total pressure while keeping the temperature of the semiconductor substrate at  $450^{\circ}\text{C}$  or lower, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the lower part electrode layer, the metal oxide dielectric film, and the capacitor upper part electrode layer to obtain a capacitor with a three-layered laminated structure.

[0032]

The present invention further relates to a method for fabricating a semiconductor device, comprising: a step of forming a MOS-type transistor on a semiconductor substrate, a step of forming a first interlayer insulation film on the transistor, a step of forming electric conduction by opening a contact reaching the diffusion layer of the MOS-type transistor in the first interlayer insulation film and burying a metal plug in the contact, a step of forming a capacitor lower part electrode layer on the whole surface of the first interlayer insulation film having the metal plug, a step of forming a capacitor lower part electrode on the metal plug by patterning the capacitor lower part electrode, a step of forming a metal oxide dielectric film on the patterned capacitor lower part electrode and on the whole

surface of the first interlayer insulation film using organometal gases and an oxidizing gas at  $1 \times 10^{-4}$  Torr or higher to  $1 \times 10^{-2}$  Torr or lower of the total pressure while keeping the temperature of the semiconductor substrate at  $450^{\circ}\text{C}$  or lower, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the capacitor upper part electrode layer to obtain a capacitor with a three-layered laminated structure of the capacitor lower part electrode, the metal oxide dielectric film, and the capacitor upper part electrode.

[0033]

The present invention further relates to a method for fabricating a semiconductor device, comprising: a step of forming a MOS-type transistor on a semiconductor substrate, a step of forming a first interlayer insulation film on the transistor, a step of forming electric conduction by opening a contact reaching the diffusion layer of the MOS-type transistor in the first interlayer insulation film and burying a metal plug in the contact, a step of forming an aluminum wiring electrically connected to the metal plug on the first interlayer insulation film, a step of forming a second interlayer insulation film on the aluminum wiring, a step of forming electric conduction by opening a contact reaching the aluminum wiring in the second interlayer

insulation film and burying a metal plug, a step of forming a capacitor lower part electrode layer on the whole surface of the second interlayer insulation film including the metal plug, a step of forming a metal oxide dielectric film on the whole surface of the capacitor lower part electrode layer using organometal gases and an oxidizing gas at  $1 \times 10^{-4}$  Torr or higher to  $1 \times 10^{-2}$  Torr or lower of the total pressure while keeping the temperature of the semiconductor substrate at  $450^{\circ}\text{C}$  or lower, a step of forming a capacitor upper part electrode layer on the whole surface of the metal oxide dielectric film, and a step of patterning the capacitor lower part electrode layer, the metal oxide dielectric film, and the capacitor upper part electrode layer to obtain a capacitor with a three-layered laminated structure.

[0034]

The foregoing aluminum wiring may be formed in multilayers.

[0035]

Inventors of the present invention have found that the film formation at a low temperature is possible by controlling the total pressure to be  $1 \times 10^{-2}$  Torr or lower at the time of film formation in the case of forming a metal oxide dielectric film on a capacitor electrode using organometal gases and further that the film formation of a highly excellently oriented film is possible.

[0036]

That is, within the foregoing pressure range, even at a temperature of 450°C or lower, approximately 100% of PZT has been found oriented in the PZT(100) direction. The temperature is, as compared with the film formation temperature of a conventional method, a low film formation temperature by about 150°C or more. Consequently, for example, film formation can be carried out without oxidation of W, TiN or the like formed in the contact plug and fusion of an Al wiring formed on a substrate. As a result, by a vapor phase growth method of the present invention, a metal oxide dielectric film with uniform orientation can be formed on a semiconductor substrate on which a TiN or W layer and an Al wiring is formed.

[0037]

The reason why a crystal with uniform orientation is formed without increasing the temperature, inventors of the present invention presume as follows. Inventors of the present invention suppose whether formation of a crystal with uniform orientation is possible or not depends on the frequency of the collision of molecules of organic metal gases and an oxidizing gas. That is, if the total pressure of a vacuum chamber is  $1 \times 10^{-2}$  Torr or higher, molecules of organic metal gases and an oxidizing gas repeat collision a large number of times before they reach the substrate and fine crystals with uncontrolled

compositions are formed and the fine crystals become causes of disorder of the crystal structure and therefore, it can be supposed that if the pressure is in a range of  $1 \times 10^{-2}$  Torr or lower, such fine crystal formation can practically be suppressed and the crystal structure tends to easily be uniform even at a low temperature.

[0038]

However, in order to obtain a practically applicable film formation rate, the film formation is preferable to be carried out at higher than  $1 \times 10^{-4}$  Torr and most preferable to be carried out at a pressure within a range from  $1 \times 10^{-3}$  Torr to  $1 \times 10^{-2}$  Torr.

[0039]

Incidentally, the organometal gases mean raw material gases of organometals necessary to form a desired ferroelectric film or a high-dielectric-constant film on a capacitor electrode. For example, in the case of a PTZ film, examples of the organometal gases include gases of lead bis(dipivaloylmethanate) ( $\text{Pb}(\text{DPM})_2$ ), tetra(tert-butoxy) zirconium ( $\text{Zr}(\text{OtBu})_4$ ), tetra(isopropoxy) titanium ( $\text{Ti}(\text{OiPr})_4$ ), and the likes. In the case of a BST film, examples include gases of barium bis(dipivaloylmethanate) ( $\text{Ba}(\text{DPM})_2$ ), strontium bis(dipivaloylmethanate) ( $\text{Sr}(\text{DPM})_2$ ), tetra(isopropoxy) titanium ( $\text{Ti}(\text{OiPr})_4$ ), and the likes.

[0040]

Further, the inventors of the present invention

have found that the total pressure of the gases of a vacuum chamber decreases more, the film thickness in the plane becomes more even. Especially, it has been found that by suppressing the total pressure to  $1 \times 10^{-2}$  Torr or lower, the in-plane evenness (the difference between the thickest film thickness and the thinnest film thickness) is controlled to a degree as high as about 5% in the case of 6-inch wafers.

[0041]

Further, the inventors of the present invention have studied of correlation of the stepped-surface coating capability to the total pressure of the gases in a vacuum chamber. Investigation was carried out by experimentally forming a film on a substrate with grooves of 500 nm height and 500 nm width. The ratio of film thickness on the upper face and of the film thickness on the side faces of the grooves was measured to evaluate the film thickness evenness (the stepped-surface coating capability). As a results, when the total pressure is  $1 \times 10^{-2}$  Torr or lower, the film thickness ratio exceeds 0.75 and a significantly high stepped-surface coating capability is obtained .

[0042]

An oxidizing gas is an essential component to allow organometal gases to be deposited on a capacitor film in state that these gases are sufficiently oxidized. The kinds of the oxidizing gases can properly be selected

responding to the raw material gases as to prevent inconvenience such as alloying of each organometal gas owing to reduction of the gas on the surface of a capacitor electrode. For examples, the oxidizing gases include gases of  $O_2$ ,  $NO_2$ , ozone, oxygen radical, oxygen ion, and the likes. Among these, those with high oxidizing force are preferable and, in terms of example,  $NO_2$  is preferable.

[0043]

Since an oxidizing gas has oxidizing force to organometal gases as just described, in order to quantitatively introduce respective gases into a vacuum chamber, respective gases are required to be separately introduced so as to keep respective gases from one another.

[0044]

By controlling the gas supply conditions of respective organometal gases or oxidizing gas or both of these gases, film formation is made possible in self-controlling gas supply conditions as to provide a metal oxide dielectric film with a prescribed composition and a crystal structure.

[0045]

Regarding the flow rate of the respective raw materials of organometal gases and an oxidizing gas, there exists a self-controlling flow rate ratio as to allow the crystal structure to spontaneously have the

perovskite type crystal structure and flow control may be carried out within the range. Regarding also the flow rate of an oxidizing gas, if the flow rate is low, the oxidizing force is insufficient to organometal gases and metals themselves are possibly deposited and hence, as same in the case of organometal gases, it is preferable to carry out film formation while controlling the flow rate in a flow rate range in which the film can be provided with an evenly oriented perovskite type crystal structure.

[0046]

It is preferable for a method for introducing organometal gases into a vacuum chamber to directly control the flow rate to introduce the organometal gases without using a carrier gas. That is, introduction of a gas irrelevant to the crystal growth results in increase of the total pressure during the film formation and difficulty of formation of an evenly oriented perovskite type crystal structure and thus a formed metal oxide dielectric film cannot sufficiently show high ferroelectric properties and high dielectric properties. A method for controlling the flow rate employing a mass flow controller is one of examples of a method for directly controlling flow rate without using a carrier gas.

[0047]

Regarding a vacuum chamber, it is preferable for



the inner walls of the vacuum chamber to be controlled at not lower than a temperature at which the organometal gases can have sufficiently high vapor pressure and not higher than a decomposition temperature of the organometal gases. The reason for that is because the organometal gases and their decomposed products have to be refrained from adhering to the inner walls of the vacuum chamber and the temperature control is effective to improve the in-plane evenness of the film thickness and to suppress particle formation.

[0048]

[Modes of Execution]

Hereafter, an embodiment of the present invention will be described with reference to Figs.

[0049]

A schematic diagram of one example of a thin film vapor phase growth apparatus to be employed for the present invention is illustrated in Fig. 4. The present apparatus is composed of an exchange chamber 101, a vacuum chamber 102, and a raw material supply system 103 and a plurality of sheets of 8-inch wafers can be housed in the exchange chamber. Double gate valves 104 are installed between the vacuum chamber and the exchange chamber and the space between the two gate valves is evacuated by a pump. A wafer transferring mechanism 105 is installed for transferring wafers between the vacuum chamber and the exchange chamber. With such a

constitution, wafers can be replaced and transferred without the vacuum chamber being exposed to atmospheric air. Further, the double insertion of the gate valves is effective to suppress adhesion of the raw materials to the valve seal face and prevent leakage of atmospheric air in the vacuum chamber at the time of atmospheric air leak in the exchange chamber for replacing wafers. The exchange chamber is evacuated to  $10^{-7}$  Torr by turbopumps 106 independently installed from the pump for the vacuum chamber.

[0050]

A schematic diagram showing a part of the cross-section of the vacuum chamber is illustrated in Fig. 1. The vacuum chamber is equipped with a heater denoted with 416 and made of aluminum to be heated to a prescribed temperature. The material of the vacuum chamber is especially, aluminum, which has a high thermal conductivity, so that the inner walls of the vacuum chamber can evenly be heated.

Wafers 417 are so set on a susceptor 403 made of quartz as to keep the faces to be subjected to device formation upward. Three holes 401 with 5 mm diameter are formed in the susceptor 403 made of quartz and pins 402 made of quartz are moved up and down through the holes to mount wafers on the susceptor 403 from the transferring apparatus. After the wafers are mounted on the susceptor made of quartz, the holes for the pins are closed by the

wafers themselves. The susceptor is so put on projections projected from a wall of a vacuum chamber made of aluminum as to overlap the rim parts on the projections and in the state in which the wafers are mounted on the susceptor made of quartz, the heater chamber 405, a lower part of the wafers, and the vacuum chamber 406, an upper part, into which film growth gases are to be introduced are separated.

[0051]

The inner walls of the vacuum chamber 406 are preferable to be set at a temperature not lower than a temperature at which organometal gases can have sufficiently high vapor pressures and not higher than organometal gas decomposition temperature. That is, since organometal gases include several kinds of raw materials, the composition ratio of organometal gases reacting on the wafer could be unbalanced owing to that a part or all of the organometal gases are liquefied or solidified or that organometal gases are decomposed, so that the temperature is preferable to be controlled not lower than the temperature at which the organometal gases have sufficiently high dissociation speed without being condensed in the inner wall and lower than the decomposition temperature of the organometal gases.

[0052]

The vacuum chamber 406 and the heater chamber 405 are evacuated by separate turbo molecular pumps 407, 408

and with such a structure, the leakage of organometal gases and an oxidizing gas to the heater chamber can be suppressed. Especially, in the case of this growth method using an oxidizing gas, oxidation of the heating mechanism 409 installed in the heater chamber to heat wafers can be prevented and thus the life of the heating mechanism 409 can significantly be prolonged. Such a structure is also effective to prevent short circuit and to prevent unevenness of the substrate temperature caused by adhesion of raw material gases on the heating mechanism. The pressure of the heater chamber during the film formation was  $1 \times 10^{-6}$  Torr when the pressure of a vacuum chamber was  $1 \times 10^{-3}$  Torr and the pressure difference of about three figures was obtained.

[0053]

When the temperature of a heater for heating wafers is increased, the temperature of a susceptor made of quartz is also increased to cause adhesion of organometal gases thereon, however by coating the surface of quartz with a metal oxide (a high temperature part-coating dielectric material) of such as PTO (lead titanate:  $\text{PbTiO}_3$ ), STO (strontium titanate:  $\text{SrTiO}_3$ ), BTO (barium titanate:  $\text{BaTiO}_3$ ), PLZT  $\{(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3\}$ , PNbZT  $\{(\text{Pb}, \text{Nb})(\text{Zr}, \text{Ti})\text{O}_3\}$ , SBT ( $\text{SrBi}_2\text{TaO}_9$ ), and the likes, the parting of adhering substances of organometal gases can be suppressed and as a result, contamination with particles can be prevented.

[0054]

Two lines, a main exhaust line 410 and a sub exhaust line 411, are connected to an exhaust port of a vacuum chamber and the main exhaust line is connected to a turbo pump 407 through a main gate valve 412. The sub exhaust line 411 is connected to the turbo pump 407 through a valve 413 and then a water cooling trap 414. During the film formation, the main gate valve 412 is closed and the valve 413 is opened to discharge exhaust gases through the sub exhaust line 411. With such a constitution, solidification and liquefaction of organometal gases in the turbo pump 407 can be avoided and the life of the turbo pump 407 can be prolonged. Additionally, the total pressure of raw material gases in the vacuum chamber can be changed by introducing a valve 415 capable of adjusting conductance between the sub exhaust line 411 and the water cooling trap 414 and adjusting the conductance. At the time when no raw material gas is supplied, the exhaust speed can be heightened by opening also the main gate valve 412 to effectively maintain high vacuum degree. Further, these valves are effective to sharply decrease the partial pressure of each organometal gases in the vacuum chamber. The main gate valve 412 and the valve 413 are buried in an aluminum vacuum chamber 406 and enabled to be evenly heated.

In this apparatus, though a turbo molecular pump is

employed for a pump for exhaust, a mechanical booster pump, a dry pump, a rotary pump, or the like may be usable and it is required to plan the exhaust capability of the pump and conductance of the valves and the water cooling trap as to decrease the inner pressure of the vacuum chamber to  $1 \times 10^{-2}$  Torr or lower.

[0055]

A schematic diagram of a part of a raw material supply system is illustrated in Fig. 5. An organometal gas is a solid or a liquid at a room temperature and stored in a cylinder 501. The cylinder 501 is equipped with a valve 502 installed above and enabled to be parted from a flange 503 between the valve 502 and the supply system to exchange raw materials. Each organometal gas is extremely easily oxidized, so that the organometal gas is preferable to be kept no contact with atmospheric air. If being exposed to atmospheric air, the organometal gas is oxidized, a metal oxide is formed, the pipes are clogged, and a mass flow controller 504 is clogged.

[0056]

Organometal gases include those in a liquid state and those in a solid state at a normal temperature and normal pressure and the liquid raw materials are poured in cylinders as they are. On the other hand, solid raw materials are preferable to be deposited on the surface of alumina with about 1 mm diameter. By using such raw materials, gases can be generated stably at the time of

heating. The purity of the generated gases is high. The heating temperature of a cylinder is set to be a temperature high enough to obtain a sufficiently high vapor pressure to operate the mass flow controller.

[0057]

A pipe from the cylinder 501 is connected to the mass flow controller 504 through a stop valve 505 and thereafter divided into two pipes equipped with stop valves 506, 507, respectively, and connected to a vacuum chamber 508 and to a pump 512 via a water cooling trap 509, respectively. Parts of the raw material supply system comprising these pipes, the mass flow controller 504, valves 502, 505, 506, 507, and the likes and which are to be brought into contact with organometal gases are, as the same as the inner walls of the foregoing vacuum chamber, kept at a temperature not lower than the temperature at which the organometal gases are liquefied or solidified and not higher than the decomposition temperature of each organometal gas.

[0058]

At the time of film formation, at first the valve 502, 505, 506 are opened to operate the mass flow controller 504 by the spontaneous pressure of an organometal gas in the cylinder 501 and a gas is evacuated by the pump 512 to stabilize the gas flow rate in the mass flow controller 504 during the time. Next, the valve 506 is closed and the valve 507 is opened, so

that the organometal gas whose flow rate is precisely controlled can be supplied to the vacuum chamber.

In this embodiment, each of organometal gases and an oxidizing gas is introduced into a vacuum chamber through independent raw material supply pipes and then mixed to one another in the vacuum chamber. That is, the apparatus is so composed as to keep separated of the organometal gases and the oxidizing gas from each other before they are introduced into the vacuum chamber. The reason for that is, because if the organometal gases and the oxidizing gas are brought into contact with each other, the organometal gases are oxidized and metal oxides are generated to cause clogging of the pipes and clogging of the mass flow controller and further because the metal oxides are sent to the vacuum chamber to result in generation of particles and inhibition of thin film formation with excellent crystallinity at low temperature.

[0059]

The partial pressure of each organometal gas in the vacuum chamber is determined by the supply amount of each gas, the amount consumed on the substrate and the susceptor, the exhaust amount, and the adhesion amount to the walls of the vacuum chamber. If the temperature of the walls of the vacuum chamber is kept at a proper temperature to keep a sufficiently high vapor pressure of each organometal gas and to inhibit decomposition of each organometal gas, the decrease owing to the adhesion of



the raw material gases to the inner walls of the vacuum chamber can be neglectable. Further since the raw material gas amount consumed on the substrate and the susceptor is as low as about 1/1000 of the supply amount, the pressure of the vacuum chamber is determined by the gas supply amount and the exhaust amount. A vacuum gauge 510 for monitoring the pressure is installed in the vacuum chamber. Incidentally, the foregoing parts which are to be brought into contact with organometal gases are required to be parts having sufficiently high heat resistance to the temperature at which at least organometal gases can have sufficient vapor pressure.

[0060]

By providing an apparatus with the above described apparatus constitution, only organometal gases and an oxidizing gas necessary for film formation can be introduced into the vacuum chamber to actualize the film formation conditions of the present invention. That is, an oxidizing gas and each organometal gas can be introduced into the vacuum chamber through separate introduction ports and the pressure can be controlled to keep the inner pressure of the vacuum chamber at  $1 \times 10^{-2}$  Torr or lower. The pressure of the vacuum chamber may be changed and adjusted to be at a desired value by adjusting the exhaust amount of the sub exhaust line 411 and the flow rate of the mass flow controller. Further, by adjusting the temperature of the heater 416 to be at a

prescribed temperature, it is made possible to control the temperature of the inner walls of the vacuum chamber not lower than the temperature at which the organometal gases have sufficiently high vapor pressure and lower than the decomposition temperature of the organometal gases. In this apparatus example, aluminum, which is a material having a high thermal conductivity, is used as a material for the vacuum chamber and if the temperature to provide sufficient vapor pressure of organometal gases exceeds 200°C, a stainless steel may be employed.

[0061]

Further, since the mass flow controller is operated by the spontaneous pressure of raw material gases and the likes to introduce organometal gases and the oxidizing gas into the vacuum chamber, not like a conventional method, raw materials can be transported without using a carrier gas.

[0062]

In a method for vapor phase growth on a capacitor electrode using organometal gases, nitrogen dioxide may be used as the oxidizing gas. Nitrogen dioxide may be passed through a pipe for the oxidizing gas.

[0063]

The total pressure of the vacuum chamber during the film formation can be kept at  $1 \times 10^{-2}$  Torr or lower by controlling the exhaust amount of the sub exhaust line 411 (Fig. 1) and the flow rate of the mass flow

controller 504 (Fig. 5).

[0064]

Next, an embodiment of a film formation method of the present invention will be described while exemplifying film formation of a PZT film, for example.

[0065]

Representative raw materials, raw material temperature, and temperature of a mass flow controller in the case of PZT film formation are as follows: as a Pb raw material, lead bis(dipivaloylmethanate)  $\text{Pb}(\text{DPM})_2$ , raw material temperature  $177^\circ\text{C}$ , temperature of a mass flow controller  $200^\circ\text{C}$ ; as a Zr raw material, tetra(tert-butoxy) zirconium  $\text{Zr}(\text{OtBu})_4$ , raw material temperature  $70^\circ\text{C}$ , temperature of a mass flow controller  $110^\circ\text{C}$ ; as a Ti raw material, tetra(isopropoxy) titanium  $\text{Ti}(\text{OiPr})_4$ , raw material temperature  $75^\circ\text{C}$ , temperature of a mass flow controller  $145^\circ\text{C}$ ; the mass flow temperature of  $\text{NO}_2$   $145^\circ\text{C}$ ; and the temperature of the inner walls of the vacuum chamber  $180^\circ\text{C}$ .

[0066]

X-ray diffraction spectra of PZT in the case of keeping the film formation conditions constant and changing the film formation temperature are shown in Fig. 6. Silicon wafers employed for substrates were those produced by forming a 500 nm thick silicon oxide film on silicon wafers and then forming a 200 nm thick Pt film by a sputtering method. The film formation conditions were

controlled as follows: film formation was carried out at first for 40 seconds in the conditions of 0.2 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.05 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.25 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$ , and then film formation was carried out for 600 seconds in the conditions of 0.25 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.225 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.2 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$ . The total pressure of the gases in a vacuum chamber during the film growth was controlled to be  $5 \times 10^{-3}$  Torr.

[0067]

As being understood from Fig. 6, x-ray diffraction peak attributed to PZT with the perovskite type crystal structure were observed at 400°C substrate temperature. Though being not shown in Figs. 8, no peak attributed to PZT was observed at all at 350°C substrate temperature and it was found that the film was in amorphous state. In the present invention, film formation is preferable to be carried out at 360°C or higher and, for example, at 380°C, a PZT film with sufficiently evenly oriented crystal structure was obtained. In this Figs., the x-ray diffraction spectra obtained in the case of employing film formation temperature at three levels; 400°C, 500°C, and 600°C were compared to one another. As being shown in the Figs., in a high temperature region of 500°C or higher, two kinds of peaks of (100) and (101) were observed, whereas in a low temperature region of around

400°C, only one kind peak of (100) was observed, implying that to form a film at a low temperature was effective to obtain a film with extremely even crystallization direction and with a highly oriented perovskite type crystal structure. Also in the case of forming a film at a temperature lower than 400°C, as long as the temperature was high enough to form a perovskite type crystal structure, the patterns of the x-ray diffraction spectra of the resultant films were same as those of films formed at 400°C and only one kind peak of (100) was observed to find that films formed had extremely even crystallization direction and with a highly oriented perovskite type crystal structure.

[0068]

Fig. 7 shows the alteration of the ratio of crystal grains whose crystal axes in the perpendicular direction to a substrate was (100) in polycrystalline PZT computed from the x-ray diffraction spectra in the case of changing the film formation temperature. From Fig. 7, it was found that films so highly oriented as to orient all of the crystal grains to the (100) direction were obtained by controlling the film formation temperature at 450°C or lower. At 450°C or higher, crystal grains oriented in the (101) or (111) direction were formed to find the orientation property was deteriorated.

[0069]

The crystallization temperature as shown has

noticeable total pressure dependency. In Fig. 8, the alteration of the height of the PZT (100) peak appearing in the x-ray diffraction spectra in the case of changing the total pressure without changing the ratio of the partial pressure of each organometal gas by adjusting the conductance valve 415 installed in the foregoing sub exhaust line while keeping the substrate temperature at 400°C. Silicon wafers employed for substrates were those produced by forming a 500 nm thick silicon oxide film on silicon wafers and then forming a 200 nm thick Pt film by a sputtering method. The film formation conditions were controlled as follows: film formation was carried out at first for 40 seconds in the conditions of 0.2 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.05 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.25 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$ , and then film formation was further carried out until the film thickness became 100 nm in the conditions of 0.25 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.225 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.2 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$ . The thickness of the grown film was 100 nm in this case. When the total pressure of the gases was higher than  $10^{-2}$  Torr, the height of the PZT(100) peak was found sharply decreasing. That shows if the total pressure is higher than  $10^{-2}$  Torr, the crystal structure becomes deteriorated from the perovskite type crystal structure of PZT (100) with desired orientation property. In a high pressure region

of the total pressure higher than  $10^{-2}$  Torr, peaks attributed to  $\text{PbO}$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  are observed in x-ray diffraction spectra.

[0070]

The reason why the crystallinity is better as the pressure in a vacuum chamber is decreased more at the time of film formation is based on the following principle. When the total pressure is increased, organometal gas molecules supplied to a growth chamber repeat collision to an oxidizing gas such as nitrogen dioxide many times before they reach a substrate and decomposed by reaction to form metal oxides such as  $\text{PbO}$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  in vapor phase. Further, these metal oxides repeat collision to one another to form microcrystals of their mixtures before they reach the substrate. These microcrystals are not controlled in the compositions and the film formation temperature, so that the microcrystals cannot become the perovskite type crystal structure. If these microcrystals adhere to the substrate, crystal growth with crystal structure different from the perovskite type crystal structure starts using these microcrystals as crystal nuclei. Consequently, the crystallinity after the film formation is deteriorated. In order to rearrange these crystallines to form a perovskite type metal oxide dielectric film, the temperature has to be raised to  $650^\circ\text{C}$  or higher. Since the foregoing reaction more hardly occurs as the pressure

of the vacuum chamber is decreased more at the time of film formation, the crystallinity can be improved. However, in order to form microcrystals of mixtures, collision is required to be repeated a plurality of times and according to the foregoing experiments, if the film formation is carried out at a pressure not higher than  $10^{-2}$  Torr, reaction of an oxidizing gas and organometal gases does not take place and decomposition of the gases occurs only on the surface of a substrate and as a result, a film with excellent crystallinity can be obtained at a low temperature.

[0071]

Fig. 9 shows the alteration of the height of the PZT (100) peak appearing in the x-ray diffraction spectra in the case of keeping the substrate temperature at 400°C and introducing argon into a vacuum chamber and changing the introduction quantity of argon without changing the flow rate of each organometal gas and the exhaust rate. Silicon wafers employed for substrates were those produced by forming a 500 nm thick silicon oxide film on silicon wafers and then forming a 200 nm thick Pt film by a sputtering method. The film formation conditions were controlled as follows: film formation was carried out at first for 40 seconds in the conditions of 0.2 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.05 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.25 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$ , and then film formation was carried out for 600



seconds in the conditions of 0.25 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.225 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.2 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$ . The total pressure of the gases in a vacuum chamber during the film growth was controlled to be  $5 \times 10^{-3}$  Torr. The formed film thickness was 100 nm at that time. It was found that in the case the introduction amount of argon was much, the PZT(100) peak was low and that if the introduction amount of argon was decreased, the PZT(100) peak was increased. This is also observed in the same manner in the case of introducing a gas to be used as a carrier gas irrelevant to film growth such as nitrogen and helium. Therefore, it is found effective to avoid simultaneous introduction of such carrier gases in order to obtain excellent crystals at a low temperature.

[0072]

The present invention is also significantly effective to improve property deterioration at the time of making a film thin. That is based on the following principle. By a conventional method such as a sol-gel method or the like, crystallization is caused by heating at a temperature as high as  $600^\circ\text{C}$  or higher. At that time, metals of a metal oxide dielectric film are alloyed with an electrode metal and diffused in the electrode metal. For example, in the case of PZT, Pb is diffused into the electrode, so that lead voids where Pb is deficient are formed in the vicinity of the interface.

Such a part where a part of metals is lessened is called as a transition layer. The transition layer is a film as thin as about 1,000 Å or thinner and in a region of about several thousand Å or less in the thickness direction including the transition layer, the composition differs from the stoichiometric ratio and the orientation is inferior to result in inferior electric properties. In the case where a film is made thin, the ratio of the transition layer in the film increases to result in deterioration of properties. However, in this method of the present invention, since film formation is carried out at 450°C or less, such a transition layer is scarcely formed and deterioration of the properties in the case of thinning a film is scarce.

[0073]

Fig. 10 shows the dependency of the spontaneous polarization on the film thickness, where PZT film formation was conducted by a vapor phase growth method of the present invention. Silicon wafers employed for substrates were those produced by forming a 500 nm thick silicon oxide film on silicon wafers and then forming a 200 nm thick Pt film by a sputtering method. The film formation conditions were controlled as follows: film formation was carried out at first for 40 seconds in the conditions of 0.2 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.05 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.25 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$ , and then film formation

was carried out for 600 seconds in the conditions of 0.25 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.225 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.2 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$ . The total pressure of the gases in a vacuum chamber during the film growth was controlled to be  $5 \times 10^{-3}$  Torr. The obtained film thickness in this case was 100 nm. As compared with results of spontaneous polarization of a dielectric film formed by a sol-gel method as shown in Fig. 3, it was found that the spontaneous polarization value did not decrease even in the case of thin films. The similarly improvement effect was confirmed in suppression of specific dielectric constant in a high-dielectric-constant film of such as BST.

[0074]

By using nitrogen dioxide as an oxidizing gas, the oxidizing force of the oxidizing agent is improved during the film formation and the properties of a film can be further improved. Figs. 11 shows the comparison of x-ray diffraction spectra of the cases of using  $\text{O}_2$  and  $\text{NO}_2$  as oxidizing agents in PZT film formation at  $400^\circ\text{C}$  substrate temperature and in the same conditions. The flow rates of  $\text{O}_2$  and  $\text{NO}_2$  were so controlled as to keep the total pressure  $5 \times 10^{-3}$  Torr or less and kept at the same flow rate. As being understood according to the Figs. 11, though PZT crystal was formed in both cases, in the case of using  $\text{O}_2$ , the PZT(100) peak value was low and the

crystallinity was inferior. Also in the case of using  $O_2$ , a peak attributed to  $PbPt_x$ , which was an alloy of Pt and Pb, appeared in the low angle side of Pt and that was supposedly attributed to that Pb was insufficiently oxidized and metal Pb was deposited and alloyed with Pt. According to the results of investigation of the compositions of specimens by fluorescence x-ray analysis, it was found that owing to the alloying with Pt, Pb was deficient and also that oxygen amount was low. In the case of supplying ozone as an oxidizing agent from an ozone generating apparatus installed in the outside of the apparatus or further same in the case of installing a plasma source of such as ECR in the film formation chamber to dissociate oxygen in plasma and supply oxygen radical or oxygen ion as an oxidizing agent, it was found that the oxidizing force was improved as compared with that in the case of supplying oxygen molecule, alloying reaction with Pt was suppressed, and the oxygen deficiency in a resultant film could be suppressed.

[0075]

Fig. 12 shows the alteration of the composition ratios of Zr/Pb, Ti/Pb in the case of altering the flow rate of  $NO_2$  while keeping the flow rates of organometal gases of Pb, Zr, and Ti constant. That is, as film formation conditions, the substrate temperature was set at  $400^\circ C$  and film formation was carried out at first for 40 seconds in the conditions of 0.2 SCCM flow rate of

Pb(DPM)<sub>2</sub>, 0.05 SCCM flow rate of Zr(OtBu)<sub>4</sub>, 0.25 SCCM flow rate of Ti(OiPr)<sub>4</sub>, and flow rate of NO<sub>2</sub> changed to be the flow rate as shown in Fig. 14 and then film formation was further carried out for 600 seconds in the conditions of 0.25 SCCM flow rate of Pb(DPM)<sub>2</sub>, 0.225 SCCM flow rate of Zr(OtBu)<sub>4</sub>, 0.2 SCCM flow rate of Ti(OiPr)<sub>4</sub>, and flow rate of NO<sub>2</sub> changed to be the flow rate as shown in Fig. 14. The total pressure of the gases in the vacuum chamber during the film formation was controlled to be  $5 \times 10^{-3}$  Torr. At 2 SCCM or higher NO<sub>2</sub> flow rate, the resultant compositions were found well conformed to the stoichiometric ratio and perovskite type crystals with even orientation were found produced. At 1.5 SCCM or lower flow rate of NO<sub>2</sub>, Ti/Pb, Zr/Pb increased and it was found that the crystal structure was slightly deteriorated. That was attributed to that since the oxidizing force to Pb was insufficient at 1.5 SCCM or lower flow rate of NO<sub>2</sub>, the deposition of metal Pb and subsequent alloying with Pt took place so that Pb was removed from the films. The total pressure in the vacuum chamber at that time was  $1 \times 10^{-4}$  Torr. It is, therefore, preferable to carry out film formation in a range of flow rates of an oxidizing gas to provide sufficient oxidizing force.

[0076]

As described above, NO<sub>2</sub> has high oxidizing force to Pb, and as compared with O<sub>2</sub>, since the supply amount can

be decreased,  $\text{NO}_2$  is significantly efficient for film formation in a low pressure region.

[0077]

Fig. 13 shows the correlation between the total pressure and the film formation rate. The Fig. shows the PZT film formation rate in the case of changing the total pressure without changing the partial pressure of each raw material gases by adjusting the conductance valve 415 installed in the sub exhaust line 414 in Fig. 1. It was found that as the ambient gas became thinner, the film formation rate was decreased more owing to the decrease of the raw material supply amounts to the substrate surface. Being understood from this Fig., practically applicable film formation rate can be obtained if the total pressure is  $1 \times 10^{-4}$  Torr or higher.

[0078]

A method of the present invention can provide excellent results on the in-plane evenness of the film thickness. Fig. 14 shows the in-plane distribution of the film thickness in a 6-inch wafer in the case of changing the total pressure without changing the ratio of the partial pressure of each organometal gas by adjusting the conductance valve installed in the sub exhaust line. It was found that as the pressure was decreased, the in-plane distribution of the film thickness was improved and that such an effect was significant at  $1 \times 10^{-2}$  Torr or lower. Further, the in-plane evenness of the film

thickness was greatly affected with the temperature of the inner walls of the vacuum chamber.

[0079]

Fig. 15 shows the alteration of the in-plane distribution of the film thickness in the case of changing the temperature of the inner walls of the vacuum chamber. The increase of the temperature of the inner walls of the vacuum chamber was found effective to the improvement the in-plane distribution of the film thickness. In the case of increasing the temperature of the inner walls of the vacuum chamber to 175°C or higher, adhesion of organometal gases to the inner walls could be suppressed and the distribution of the organometal gases in the vacuum chamber became even to result in the improvement of the in-plane distribution of the film thickness.

[0080]

Next, a method for controlling the composition of the present film formation will be described.

Fig. 16 illustrates the alteration of the composition ratio of (Ti + Zr)/Pb in films. Film formation of these films are first conducted for 40 seconds under the conditions of 0.2 SCCM flow rate of Pb(DPM)<sub>2</sub>, 0.05 SCCM flow rate of Zr(OtBu)<sub>4</sub>, 0.25 SCCM flow rate of Ti(OiPr)<sub>4</sub>, and 3.0 SCCM flow rate of NO<sub>2</sub>; and then the flow rate of the raw material for Pb was changed while constantly keeping the conditions of 0.225

SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.2 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$ . And the change of  $(\text{Ti} + \text{Zr})/\text{Pb}$  in the resulting films was measured. The total pressure of the gases in a vacuum chamber during the film growth was controlled to be  $5 \times 10^{-3}$  Torr. A substrate produced by forming a 200 nm thick Pt film on a silicon wafer bearing a 500 nm thick silicon oxide film thereon by sputtering was employed as a substrate. The duration of the film formation was set for 600 seconds and the thickness of the grown film was about 100 nm. The composition ratio were computed based on composition analysis by fluorescence x-rays. It was understood that the composition ratio reached the stoichiometric ratio when the flow rate of Pb was 0.15 SCCM; and that the stoichiometric ratio thereafter was kept by increasing the Pb flow rate even to 0.25 SCCM to prove formation of a crystal with a perovskite type crystal structure with even orientation. In such a manner, it can be understood that self-controlling film formation is possible to conform the composition of A, B sites, that is, Pb with Zr and Ti to the stoichiometric ratio in prescribed film formation conditions. That is based on the following principle. The Pb organometal gas is decomposed on the PZT surface and oxidized to  $\text{PbO}$ . The adhesion coefficient of  $\text{PbO}$  on the PZT is low and hence no film formation occurs only by passing the Pb organometal gas to the PZT surface. If Ti and Zr are supplied,  $\text{PbO}$  on



the surface is bonded to Ti or Zr on the surface before being released to the vapor phase and immobilized on the surface. Consequently, even if a Pb raw material is supplied excessively to a certain extent, Pb which is not bonded to Ti or Zr is released in gaseous phase to result in existence of a self-control region to give a stoichiometric ratio.

The Pb raw material flow rate increases and the surface density of PbO increases, so that reaction of PbO molecules themselves takes place on the surface to result in PbO crystal formation and sharp increase of Pb composition due to the strong adhesion of PbO to PbO. In order to achieve such a self-controllability, it is required to carry out film formation at  $10^{-2}$  Torr or lower and to decompose gases on the surface. If the total pressure exceeds  $10^{-2}$  Torr, reaction is caused in the vapor-phase and microcrystals are formed and re-evaporation of PbO hardly takes place to make self-control of the composition difficult.

[0081]

By a method of the present invention, the Ti/Zr ratio in a film was controlled by the ratio of the flow rate of organometal gases of Ti and Zr. Fig. 17 shows the alteration of the Ti/Zr composition ratio in the film in the case of changing the flow rate of the Ti raw material in film formation carried out at first for 40 seconds in the conditions of 0.2 SCCM flow rate of

Pb(DPM)<sub>2</sub>, 0.05 SCCM flow rate of Zr(OtBu)<sub>4</sub>, 0.25 SCCM flow rate of Ti(OiPr)<sub>4</sub>, and 3.0 SCCM flow rate of NO<sub>2</sub> and then further carried out in the conditions of keeping 0.25 SCCM flow rate of Pb(DPM)<sub>2</sub>, 0.225 SCCM flow rate of Zr(OtBu)<sub>4</sub>, and 3.0 SCCM flow rate of NO<sub>2</sub> unchanged and changing the flow rate of the Ti raw material. The total pressure of the gases in a vacuum chamber during the film growth was controlled to be  $5 \times 10^{-3}$  Torr. Silicon wafers employed for substrates were those produced by forming a 500 nm thick silicon oxide film on silicon wafers and then forming a 200 nm thick Pt film by a sputtering method. The film formation duration was 600 seconds and the grown film thickness at that time was about 100 nm. The composition ratio was computed by composition analysis by fluorescence x-ray. As the Ti raw material flow rate was increased more, the Ti/Pb ratio was increased and the Zr/Pb ratio was decreased. The (Ti + Zr)/Pb ratio was thus kept constant and the A/B site ratio satisfied the stoichiometric ratio and a crystal with evenly oriented perovskite type crystal structure was found formed. Hence, it was proved that the Ti/Zr ratio in a film could be controlled by changing the ratio of the flow rates of the Ti raw material and the Zr raw material. Fig. 18 shows the alteration of the x-ray diffraction spectra of PZT in the case of changing the flow rate of the Ti raw material in film formation carried out at first for 40 seconds in the conditions of

0.2 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.05 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.25 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  and then further carried out in the conditions of keeping 0.25 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.225 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  unchanged and changing the flow rate of the Ti raw material. As the Ti raw material flow rate was increased more, the difference of the (100) axis length and (001) axis length of PZT becomes wide, so that it was found that the peaks of (100), (001) and (200), (002) in the x-ray diffraction spectra tended to be separated. These results also proved that the Ti/Zr ratio could be controlled by changing the flow rates of the Ti raw material and the Zr raw material.

[0082]

Fig. 19 shows the hysteresis characteristics of PZT films formed by the same conditions. In the case of low Ti, the spontaneous polarization was a low value and as Ti was increased more, the hysteresis curves rose more and spontaneous polarization was thus found increased. In general, since with the increase of the Ti amount in a PZT film, the spontaneous polarization is increased, these results also proved that the Ti/Zr ratio could be controlled by changing the flow rates of the Ti raw material and the Zr raw material. In this invention, it was further found there was caused a significant effect to control a spontaneous polarization degree of a

hysteresis curve by changing the flow rate of the Ti raw material and the Zr raw material.

[0083]

A method of the present invention can improve the stepped-surface coating capability. That is because raw materials are supplied to even to the bottom of the steps owing to a convection layer of gases scarcely exists in the low pressure region.

[0084]

Fig. 20 shows the ratio of the film thickness of the upper face and the film thickness of the side face in the case of PZT film formation on an electrode having a step of 500 nm height and 500 nm width while changing the total pressure without changing the partial pressure of each organometal gas by adjusting the conductance valve installed in the sub exhaust line. According to Fig. 20, it was found that to decrease the total pressure to  $10^{-2}$  Torr or lower was effective to improve the stepped-face coating capability.

[0085]

A method of the present invention was also effective to decrease particles. Fig. 21 shows the total number of particles in a 6-inch wafer in the case of continuously forming films on 1,000 wafers at 400°C substrate temperature while changing the total pressure without changing the ratio of the partial pressure of each organometal gas by adjusting the conductance valve

installed in the foregoing sub exhaust line in the following conditions: at first in the conditions of 0.2 SCCM flow rate of  $\text{Pb(DPM)}_2$ , 0.05 SCCM flow rate of  $\text{Zr(OtBu)}_4$ , 0.25 SCCM flow rate of  $\text{Ti(OiPr)}_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  for 40 seconds and then in the conditions of 0.25 SCCM flow rate of  $\text{Pb(DPM)}_2$ , 0.225 SCCM flow rate of  $\text{Zr(OtBu)}_4$ , 0.2 SCCM flow rate of  $\text{Ti(OiPr)}_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  for 600 seconds. It was found that when the total pressure decreased lower than  $1 \times 10^{-2}$  Torr, the number of particles was sharply decreased. That was because microcrystal nuclei were formed in the vapor phase as described above if the total pressure exceeded  $1 \times 10^{-2}$  Torr and deposited on inner walls of a vacuum chamber, a susceptor or the like to result in particle formation.

[0086]

A method of the present invention is capable of further decreasing the number of the particles by setting the temperature of the inner walls of a vacuum chamber to be not lower the temperature at which the organometal gases are allowed to have a sufficiently high vapor pressure and not higher than the temperature at which the organometal gases are decomposed. Fig. 22 shows the total number of particles in a 6-inch wafer in the case of continuously forming films on 1,000 wafers at  $400^\circ\text{C}$  substrate temperature while changing the temperature of the inner walls of the vacuum chamber in the following

conditions: at first in the conditions of 0.2 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.05 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.25 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  for 40 seconds and then in the conditions of 0.25 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.225 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.2 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  for 600 seconds. The total pressure of the gases in the vacuum chamber during the film formation was controlled to be  $5 \times 10^{-3}$  Torr. It was found that with the increase of the temperature of the inner walls of the vacuum chamber, the number of the particles tended to decrease. Such a tendency was attributed to that if the temperature of the inner walls of the vacuum chamber was decreased, organometal gases adhered to the vacuum chamber and were parted. Nevertheless, the temperature of the inner walls of the vacuum chamber should be at highest the decomposition temperature of the organometal gases and if the temperature was increased higher than that, reaction products formed by decomposition of the organometal gases adhered to the inner walls of the vacuum chamber and were parted to result in increase of particles.

[0087]

Though an embodiment of the present invention was described above while exemplifying PZT film formation, a vapor phase growth method of the present invention is not limited to the PZT film formation methods and effective

to formation of a metal oxide dielectric film whose properties can be changed by crystal orientation. The metal oxide dielectric materials for a ferroelectric or high-dielectric-constant film formable to be a film by a film formation method of the present invention include oxides having general formulas;  $\text{SrBi}_2\text{Ez}_2\text{O}_9$  (wherein Ez denotes Nb or Ta);  $\text{EpBi}_2\text{EqO}_9$  (wherein Ep denotes Ba or Pb and Eq denotes Nb or Ta);  $\text{ExBi}_4\text{Ti}_4\text{O}_{15}$  (wherein Ex denotes Sr, Ba or Pb);  $\text{Ey}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  (wherein Ey denotes Sr, Ba or Pb);  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ;  $(\text{Pb}_{1-y}\text{La}_y)(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ;  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ;  $\text{SrTiO}_3$ , and  $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ , and the metal oxide dielectric materials are not at all restricted to these materials.

[0088]

Practical examples of the foregoing ferroelectric or high-dielectric-constant metal oxide films are PTO (lead titanate:  $\text{PbTiO}_3$ ), STO (strontium titanate:  $\text{SrTiO}_3$ ), BTO (barium titanate:  $\text{BaTiO}_3$ ), PLZT  $\{(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3\}$ , PNbZT  $\{(\text{Pb}, \text{Nb})(\text{Zr}, \text{Ti})\text{O}_3\}$ , SBT ( $\text{SrBi}_2\text{TaO}_9$ ), and the likes.

[0089]

Further, in these embodiments, though the flow rate of each raw material gas was controlled by a mass flow controller, it was confirmed that a method of the present invention was effective to a method in which the pressure of a film formation chamber was controlled by further using partial pressure measuring means such as a molecular weight measuring apparatus and atomic absorption spectroscopy in the case of employing a raw

material supply system equipped with a liquid supply type flow rate controlling apparatus and an evaporator.

[0090]

A method for fabricating a memory cell relevant to the first embodiment of the present invention is illustrated in Figs. 23. At first, an oxide film was formed on a silicon substrate by wet oxidation. After that, n-type and p-type wells were formed by ion-implantation with impurities of boron, phosphorus or the like. Then, gates and diffusion layers were formed in the following manner. At first, gate oxide films 601 were formed by wet oxidation and then polysilicon 602 was formed in film state and then etching was carried out to give gates. After a silicon oxide film was formed on the resultant polysilicon layers, etching was carried out to form side wall oxidation films 603. Next, n-type and p-type diffusion layers were formed by ion implantation with impurities of boron, arsenic or the like. Further, after a Ti film was formed on the resultant layers and reacted with silicon, the unreacted Ti was removed by etching to form Ti silicide on the gates 604 and the diffusion layers 605. Through the foregoing process, as shown in Fig. 23(A), n-type and p-type MOS type transistors isolated by the oxidized film 606 for isolated were formed on a silicon substrate.

[0091]

Next, contacts and a lower part electrode were



formed as illustrated in Fig. 29(B). At first, after a silicon oxide film or a silicon oxide film (BPSG) doped with impurities such as boron was formed as a first interlayer insulation film 607, leveling was carried out by a CMP method. Following to that, after contact holes were opened by etching, the respective n-type and p-type diffusion layers were implanted with impurities and then subjected to heating at 750°C for 10 seconds. After that, Ti and TiN were formed in films as barrier metals. After tungsten layer was formed further thereon by a CVD method, plugs 608 of tungsten were formed by CMP. The plugs of tungsten might be formed by etching back after CVD of tungsten. Further thereon, as a capacitor lower part electrode layer, a Ti film 609 and a TiN film 610 were successively formed by sputtering and a 100 nm thick Pt film 611 was formed thereon.

[0092]

Next, a ferroelectric capacitor was formed as illustrated in Fig. 23(C). PZT of 100 nm thickness was formed by employing a method of the present invention. Lead bis(dipivaloylmethanate)  $\text{Pb}(\text{DPM})_2$ , titanium tetra(isopropoxide)  $\text{Ti}(\text{OiPr})_4$ , and zirconium tetra(tert-butoxide)  $\text{Zr}(\text{OtBu})_4$  were used as raw materials and  $\text{NO}_2$  was used as an oxidizing agent. A metal oxide dielectric film of PZT 612 was obtained by film formation in conditions of at 400°C of the substrate temperature and at first 0.2 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.05 SCCM flow

rate of  $\text{Zr}(\text{OtBu})_4$ , 0.25 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  for 40 seconds and then 0.25 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.225 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.2 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  for 600 seconds. The total pressure of the gases in the vacuum chamber during the film growth at that time was controlled to be  $5 \times 10^{-3}$  Torr. The thickness of the grown film was 100 nm. Then, IrO<sub>2</sub> 613 and Ir 614 were formed in films by a sputtering method to form a capacitor upper part electrode layer. Thereafter, the capacitor upper part electrode layer, the metal oxide dielectric film, and the capacitor lower part electrode layer were patterned to form isolated PZT capacitors by dry etching.

[0093]

A capacitor upper part electrode was formed thereon as illustrate in Fig. 23(D). After a silicon oxide layer was formed by a plasma CVD method as a second interlayer insulation film 615, capacitor upper part contacts and plate wire contacts were opened by etching. After WSi, TiN, AlCu, and TiN were formed in films in this order by sputtering, they were processed by etching to give a second metal wirings 616. After a silicon oxide film and a SiON film were formed thereon as passivation film 617, wiring pad parts were opened and electric properties were evaluated.

[0094]

Though, with reference to Figs. 23, description was made for the method in which isolation of capacitors were performed by dry etching after formation of the capacitor lower part electrode, the PZT film, and the  $\text{IrO}_2/\text{Ir}$  capacitor upper part electrode. However, as illustrated in Figs. 24, the method may be carried out in the following order: at first the capacitor lower part electrodes, that is,  $\text{Pt}/\text{TiN}/\text{Ti}$ , are isolated by dry etching and then the PZT film is formed, the  $\text{IrO}_2/\text{Ir}$  capacitor upper part electrode layer is formed, and after that the upper part electrodes are isolated. By this method, the film required to be dry etched is thin film. Owing to this, a finer pattern can be formed. Further, since the side faces of PZT are not exposed to plasma, introduction of defects in the PZT film can be avoided. The electric properties of the capacitors fabricated by the methods illustrated by Figs. 23 and 24 will be described below.

[0095]

5,000 of PZT capacitors with  $1\text{ }\mu\text{m}$  square were connected in parallel and the properties were measured. As a result,  $10\text{ }\mu\text{C}/\text{cm}^2$  or higher value of the difference of the inversion and non-inversion electric charge was obtained to show excellent dielectric property. The fatigue property and the retention property were also excellent. Further, by evaluation of the properties in transistors of  $0.26\text{ }\mu\text{m}$  gate length, variation of

threshold voltage values ( $V_t$ ) of both p-type and n-type was found 10% or lower in the whole surface of a wafer and found excellent. Further, by measurement of the resistance of the capacitor lower part contacts of  $0.4 \mu\text{m}$  square by a contact chain method, it was found that the resistance per single contact was  $10 \Omega\text{cm}$  or lower and excellent.

[0096]

Next, a method for fabricating memory cells relevant to the second embodiment of the present invention is illustrated in Figs. 25. Memory cells were fabricated in the same manner as the first embodiment up to the step forming tungsten plugs in the process. Further, Ti, TiN films were formed thereon. An AlCu film was formed by a sputtering method and first aluminum wirings 618 were formed by a dry etching method. By the above described process, the first aluminum wiring was formed on n-type and p-type MOS transistors as illustrated in Fig. 25(A).

[0097]

Then, via holes and second aluminum wirings were formed as illustrated in Fig. 25(B). At first, after a silicon oxide film or a silicon oxide film (BPSG) doped with impurities such as boron was formed as a second interlayer insulation film 619, leveling was carried out by a CMP method. Following to that, after via holes were opened by etching, Ti and TiN were formed in films as

barrier metals. After tungsten was formed in a film further thereon by a CVD method, plugs 620 of tungsten were formed by CMP. The plugs of tungsten might be formed by etching back after CVD of tungsten. Further thereon, Ti and TiN were formed by a sputtering method and second aluminum wirings 621 were formed by a dry etching method. Then, as a third interlayer insulation film 622, a silicon oxide film or a silicon oxide film (BPSG) doped with impurities such as boron was formed, and leveling was carried out by a CMP method. Next, via holes were opened by etching, Ti film and TiN film were formed as barrier metals. After tungsten film was formed further thereon by a CVD method, plugs 623 of tungsten were formed by CMP. The plugs of tungsten might be formed by etching back after CVD of tungsten. A desired number of wiring layers might be formed by repeating these aluminum wiring, interlayer film formation, and via hole formation. On the final tungsten plugs, a Ti film 624 and a TiN film 625 were successively formed by sputtering and a 100 nm thick Pt film 626 was formed thereon to give lower part capacitor electrodes.

[0098]

Next, a ferroelectric capacitor was formed as illustrated in Fig. 32(C). PZT of 100 nm thickness was formed by employing a method of the present invention. Lead bis(dipivaloylmethanate)  $\text{Pb}(\text{DPM})_2$ , titanium tetra(isopropoxide)  $\text{Ti}(\text{OiPr})_4$ , and zirconium tetra(tert-

butoxide)  $\text{Zr}(\text{OtBu})_4$  were used as raw materials and  $\text{NO}_2$  was used as an oxidizing agent. A metal oxide dielectric film of PZT 627 was obtained by film formation in conditions of at  $400^\circ\text{C}$  of the substrate temperature and at first 0.2 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.05 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.25 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  for 40 seconds and then 0.25 SCCM flow rate of  $\text{Pb}(\text{DPM})_2$ , 0.225 SCCM flow rate of  $\text{Zr}(\text{OtBu})_4$ , 0.2 SCCM flow rate of  $\text{Ti}(\text{OiPr})_4$ , and 3.0 SCCM flow rate of  $\text{NO}_2$  for 600 seconds. The total pressure of the gases in the vacuum chamber during the film growth at that time was controlled to be  $5 \times 10^{-3}$  Torr. The thickness of the grown film was 100 nm. After  $\text{IrO}_2$  film 628 and Ir film 629 were formed by a sputtering method to form a capacitor upper part electrode layer, the capacitor upper part electrode layer, the metal oxide dielectric film, and the capacitor lower part electrode layer were patterned to form isolated PZT capacitors by dry etching.

[0099]

A capacitor upper part electrode was formed thereon as illustrate in Fig. 26(D). After a silicon oxide film was formed by a plasma CVD method as a fourth interlayer insulation film 630, capacitor upper part contacts and plate wiring contact holes were opened by etching. After each film of  $\text{WSi}$ ,  $\text{TiN}$ ,  $\text{AlCu}$ , and  $\text{TiN}$  was formed in this order by sputtering, they were processed by etching to

give third metal wirings 631. After a silicon oxide film and a SiON film were formed thereon as a passivation film 632, wiring pad parts were opened and electric properties were evaluated.

[0100]

Even in the case where there is an aluminum wiring in the lower part, as same in the case as illustrated in Figs. 24, it may be allowed to carry out in the following order: at first the capacitor lower part electrodes, that is, Pt/TiN/Ti, are isolated by dry etching and then the PZT film is formed, the IrO<sub>2</sub>/Ir capacitor upper part electrode layer is formed, and after that, the upper part electrodes are isolated. By this method, the film required to be dry etched is thin film. Owing to this, a finer pattern can be formed. Further, since the side faces of PZT are not exposed to plasma, introduction of defects into the PZT film can be avoided.

[0101]

The electric properties of the memory cells fabricated by this second fabrication method were evaluated in the same manner as used for the memory cells fabricated by the first fabrication method.

[0102]

As a result, 10  $\mu\text{C}/\text{cm}^2$  or higher value of the difference of the inversion and non-inversion electric charge was obtained to show excellent dielectric property. The fatigue property and the retention property were also

excellent. Further, by evaluation of the properties in transistors of 0.26  $\mu\text{m}$  gate length, variation of threshold voltage values ( $V_t$ ) of both p-type and n-type was found 10% or lower in the whole surface of a wafer and found excellent. Further, by measurement of the resistance of the capacitor lower part contacts of 0.4  $\mu\text{m}$  square by a contact chain, it was found that the resistance per single contact was 10  $\Omega\text{cm}$  or less and excellent.

[0103]

Though in both cases of the first and the second embodiments relevant to the memory cells, description was given using tungsten for the contacts, also in the case of using polysilicon for the contacts, the ferroelectric capacitor property, the transistor property, and the contact resistance were all excellent as well. Further, in the examples, although description was given using Pt for the lower part electrodes, it was also confirmed that in the case of using Ir,  $\text{IrO}_2$ ,  $\text{IrO}_2/\text{Ir}$ , Ru,  $\text{RuO}_2$ , TiN, or WN, the ferroelectric capacitor property, the transistor property, and the contact resistance were all excellent as well.

[0104]

Though an example using PZT for ferroelectric capacitor formation was described, also in the case of forming  $\text{BaSrTiO}_3$  as high-dielectric-constant capacitors using  $\text{Ba}(\text{DPM})_2$ ,  $\text{Sr}(\text{DPM})_2$ ,  $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$ , and the likes, the



capacitor property, the transistor property, and the contact resistance were found all excellent completely same as those of the example.

[0105]

[Effect of the Invention]

As described above, by the present invention, a ferroelectric film and a high-dielectric-constant film with controlled orientation property can be formed at a low temperature. In addition, even if a film is made thin, the characteristics of the film are scarcely deteriorated and a film with low inversion fatigue and excellent crystallinity can be obtained. By employing the present method, ferroelectric capacitors or high-dielectric-constant capacitors can be fabricated on electrodes formed on plugs such as tungsten and polysilicon without deteriorating the plugs and wiring and transistors in the lower layers to enable significant miniaturization of the capacitor surface area and to remarkably heighten the integration degree.

[Brief Description of the Drawings]

Fig. 1 is a diagrammatic illustration showing the cross-section of a vacuum chamber of an apparatus for vapor phase growth of a thin film to be employed for the present invention;

Fig. 2 is a diagrammatic illustration showing a conventional example of a reactive gas supply method in the case of using a carrier gas;

Fig. 3 shows a graph illustrating the correlation between the film thickness and the spontaneous polarization  $2P_r$  in the case of PZT film growth on Pt using a sol-gel method;

Fig. 4 is a diagrammatic illustration of an apparatus for vapor phase growth of a thin film to be employed for the present invention;

Fig. 5 is a diagrammatic illustration showing the raw material supply system of an apparatus for vapor phase growth of a thin film to be employed for the present invention;

Fig. 6 shows x-ray diffraction spectra in the case of keeping film formation conditions constant and changing the film formation temperature;

Fig. 7 shows a graph illustrating the alteration of the ratio of crystal grains of PZT polycrystal having (100) crystal axis in the perpendicular direction to the substrate, being computed from x-ray diffraction spectra, in the case of changing the film formation temperature;

Fig. 8 shows a graph illustrating the alteration of the height of the PZT (100) peak appearing in the x-ray diffraction spectra in the case of changing the total pressure without changing the ratio of partial pressure of each organometal gas;

Fig. 9 shows a graph illustrating the alteration of the height of the PZT (100) peak appearing in the x-ray diffraction spectra in the case of keeping the substrate

temperature at 400°C and introducing argon into the vacuum chamber and changing the introduction quantity of argon without changing the flow rate of each organometal gas and the exhaust rate;

Fig. 10 shows a graph illustrating the dependency of the spontaneous polarization on the film thick in the case of PZT film formation by the vapor phase growth method of the present invention;

Fig. 11 shows a graph illustrating the comparison of x-ray diffraction spectra of the cases of using O<sub>2</sub> and NO<sub>2</sub> as oxidizing agents in PZT film formation at 400°C substrate temperature and in the same conditions;

Fig. 12 shows a graph illustrating alteration of the composition ratios of Zr/Pb, Ti/Pb in the case of altering the flow rate of NO<sub>2</sub> while keeping the flow rates of organometal gases of Pb, Zr, and Ti constant;

Fig. 13 shows the correlation between the pressure and the film formation rate at the time of film formation;

Fig. 14 shows a graph illustrating the in-plane distribution of the film thickness in a 6-inch wafer in the case of changing the total pressure without changing the ratio of the partial pressure of each organometal gas;

Fig. 15 shows a graph illustrating the in-plane distribution of the film thickness in the case of changing the temperature of the inner walls of the vacuum

chamber;

Fig. 16 shows a graph illustrating the alteration of the (Ti + Zr)/Pb composition ratio in a film in the case of altering the Pb raw material flow rate;

Fig. 17 shows a graph illustrating the alteration of the Ti/Zr composition ratio in the film in the case of changing the flow rate of the Ti raw material;

Fig. 18 shows graphs illustrating the alteration of the x-ray diffraction spectra of PZT in the case of changing the flow rate of the Ti raw material;

Fig. 19 shows graphs illustrating the alteration of the hysteresis characteristics of PZT in the case of changing the flow rate of the Ti raw material;

Fig. 20 shows a graph illustrating the alteration of the ratio of the film thickness of the upper face and the film thickness of the side face in the case of PZT film formation on an electrode having a step of 500 nm height and 500 nm width while changing the total pressure;

Fig. 21 shows a graph illustrating the total number of particles on each 6-inch wafer in the case of continuously conducting film formation on 1,000 wafers while changing the total pressure without changing the partial pressure of each organometal gas;

Fig. 22 shows a graph illustrating the total number of particles on each 6-inch wafer in the case of continuously conducting film formation on 1,000 wafers

while changing the temperature of the inner walls of the vacuum chamber;

Fig. 23 is a schematic diagram showing the fabrication process of memory cells, which is one embodiment of the present invention. This illustration especially shows the fabrication process in which three layers of a capacitor upper part electrode layer, a capacitor lower part electrode layer, and a metal oxide dielectric film are simultaneously separated;

Fig. 24 is a schematic diagram showing the fabrication process of memory cells, which is one embodiment of the present invention. These illustrations especially show the fabrication process in which a capacitor upper part electrode layer and a capacitor lower part electrode layer are separated in respective steps and a metal oxide dielectric film is left in layered state (not separated) in the memory cells;

Fig. 25 is a schematic diagram showing the fabrication process of memory cells, which is one embodiment of the present invention. These illustrations show the first half fabrication process of the memory cells in the case of especially a semiconductor device comprising memory cells having the aluminum-multilayered wiring structure;

Fig. 26 is a schematic diagram showing the fabrication process of memory cells, which is one embodiment of the present invention. These illustrations

show the latter half fabrication process of the memory cells in the case of especially a semiconductor device comprising the memory cells having the aluminum-multilayered wiring structure.

[Reference Numerals]

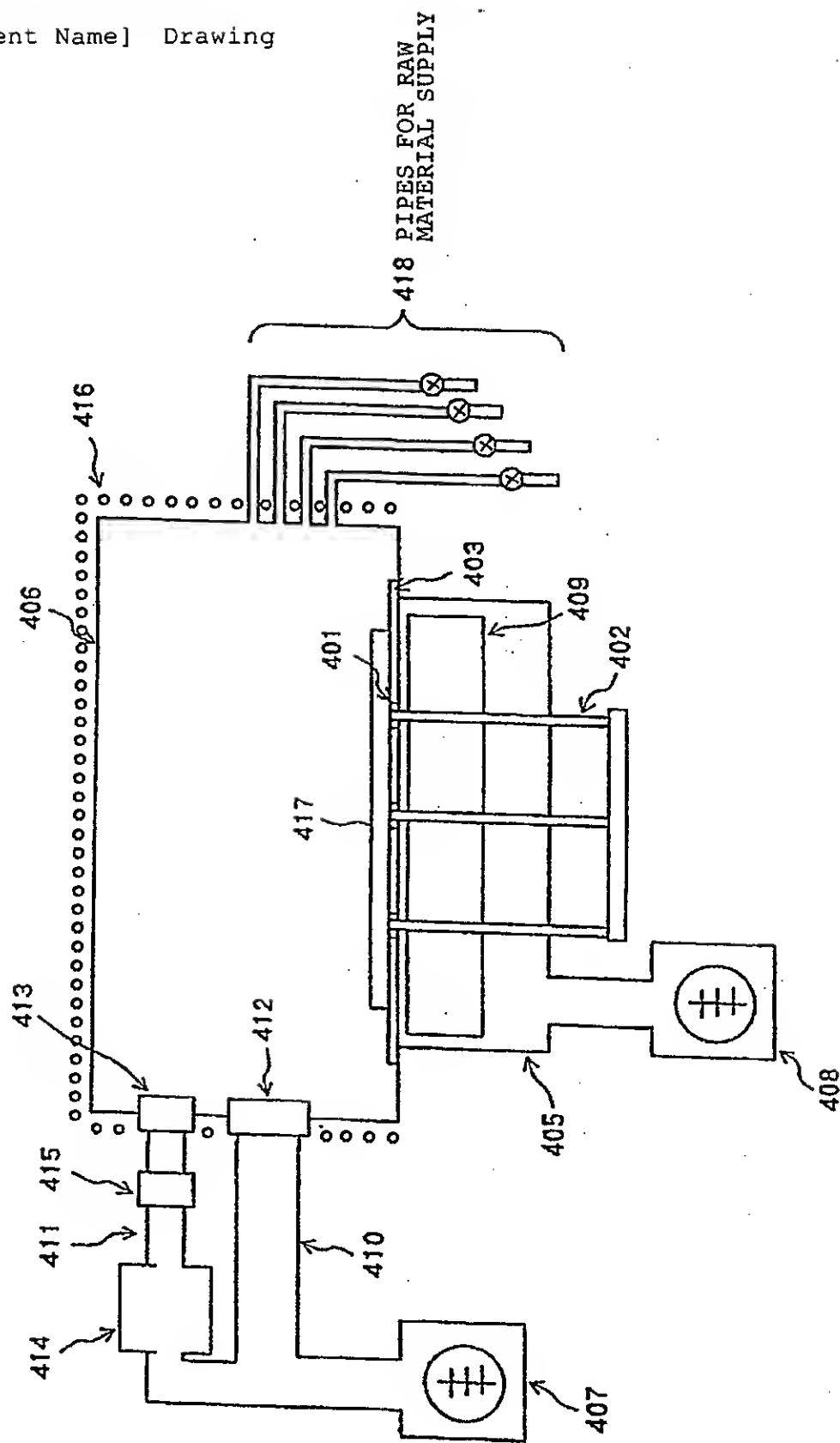
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- 102 vacuum chamber
- 103 raw material supply system
- 104 double gate valve
- 105 wafer transferring mechanism
- 106 turbo-pump
- 201 thermostat
- 202 bottle
- 203 organometal
- 204 carrier gas supply pipe
- 205 organometal material gas supply pipe
- 206 heating mechanism
- 207 growth chamber
- 208 wafer
- 209 gas exhaust
- 210 mass flow controller
- 401 hole
- 402 quartz pin
- 403 susceptor
- 405 heater chamber
- 406 vacuum chamber
- 407 turbo molecular pump

408 turbo molecular pump  
409 heating mechanism  
410 main exhaust line  
411 sub exhaust line  
412 main gate valve  
413 valve  
414 water cooling trap  
415 conductance valve  
416 heater  
417 wafer  
418 raw material supply pipe  
501 cylinder  
502 valve  
503 flange  
504 mass flow controller  
505 stop valve  
506 stop valve  
507 stop valve  
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510 vacuum gauge  
512 pump  
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602 gate polysilicon  
603 side wall oxidation film  
604 gate  
605 diffusion layer

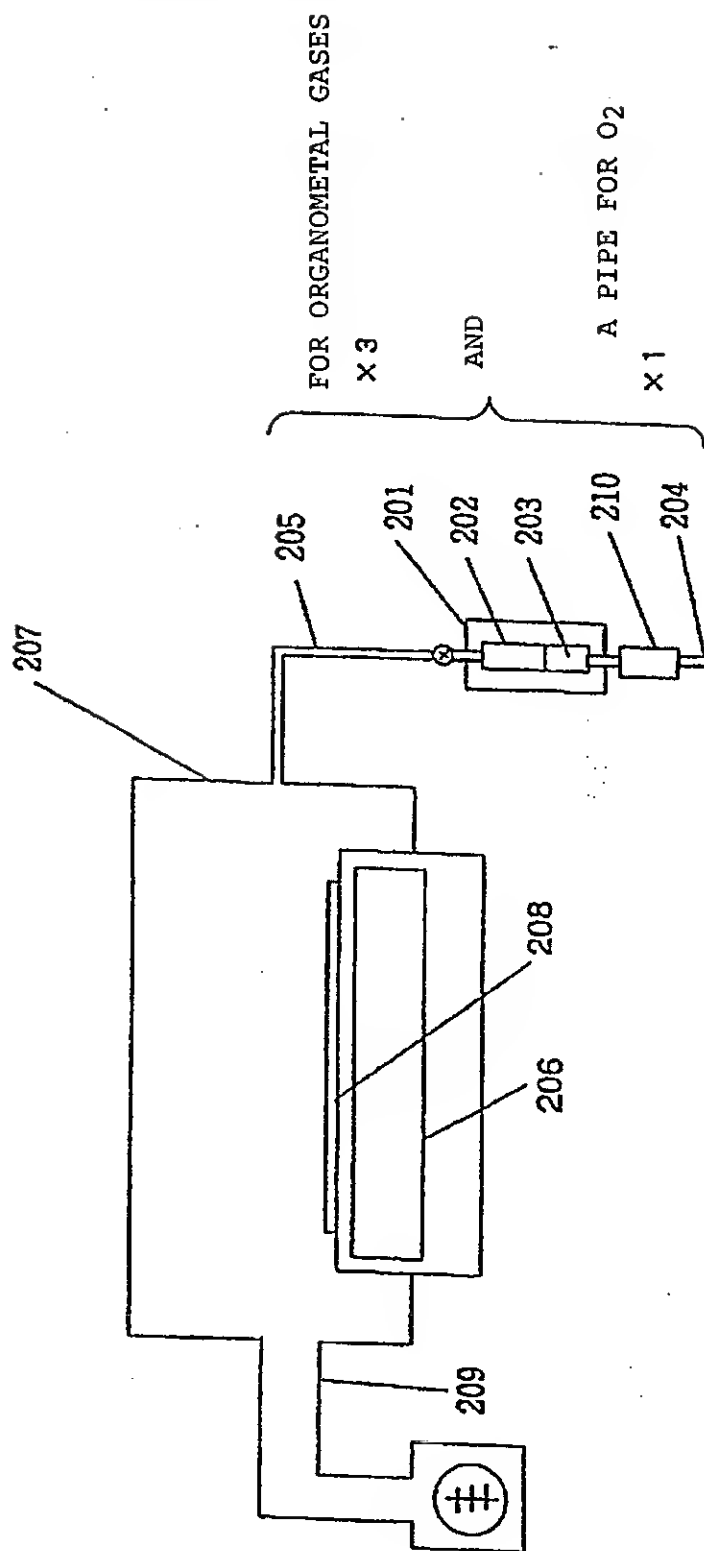
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608 tungsten lamp  
609 Ti layer  
610 TiN layer  
611 Pt layer  
612 PZT film  
613 IrO<sub>2</sub> layer  
614 Ir layer  
615 second interlayer insulation film  
616 second metal wiring  
617 passivation film  
618 first aluminum wiring  
619 second interlayer insulation film  
620 tungsten plug  
621 second aluminum wiring  
622 third interlayer insulation  
623 tungsten plug  
624 Ti layer  
625 TiN layer  
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630 fourth interlayer insulation film  
631 third metal wiring  
632 passivation film



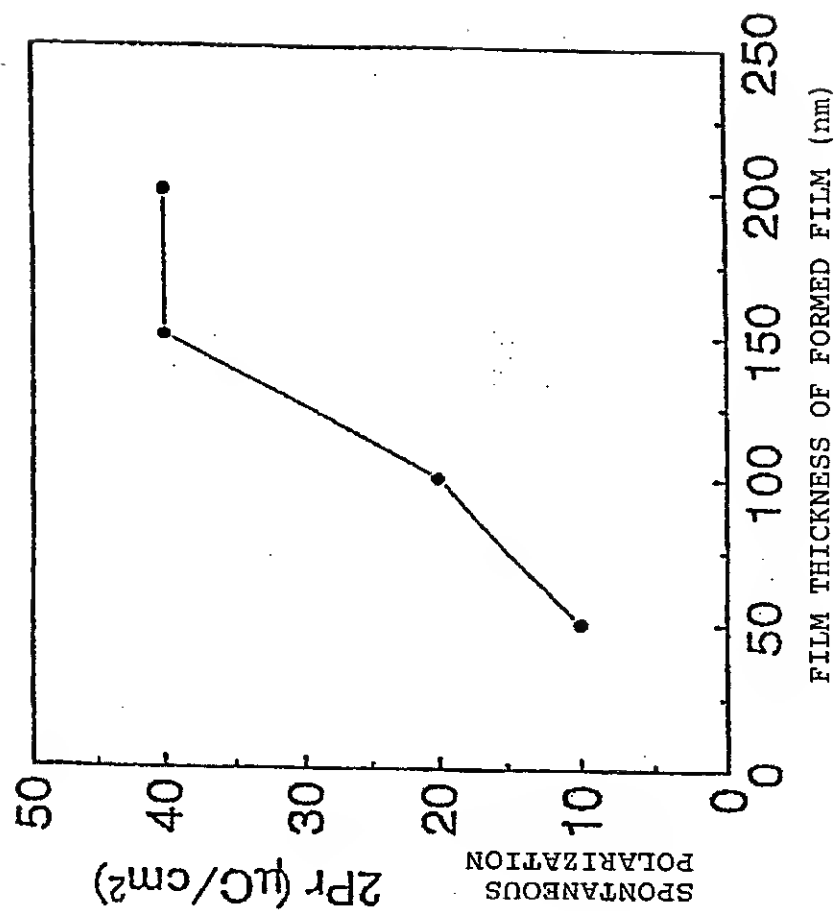
[Fig. 1]



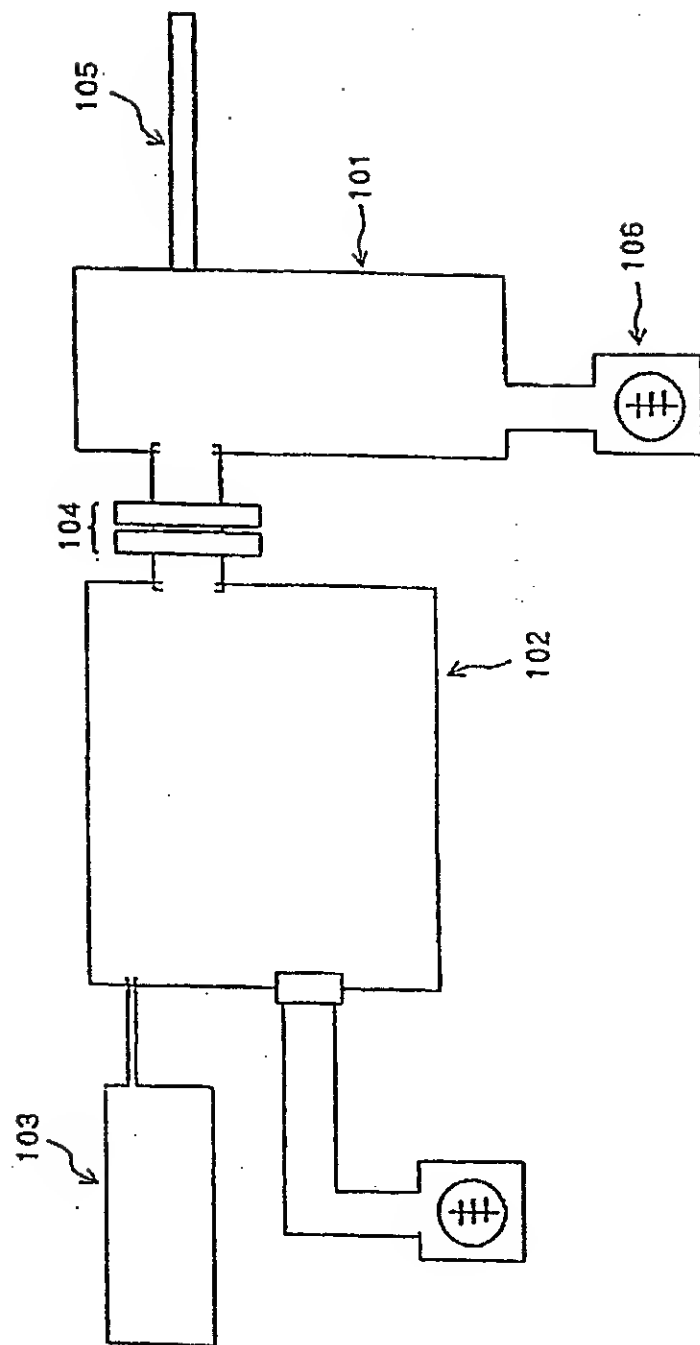
[Fig. 2]



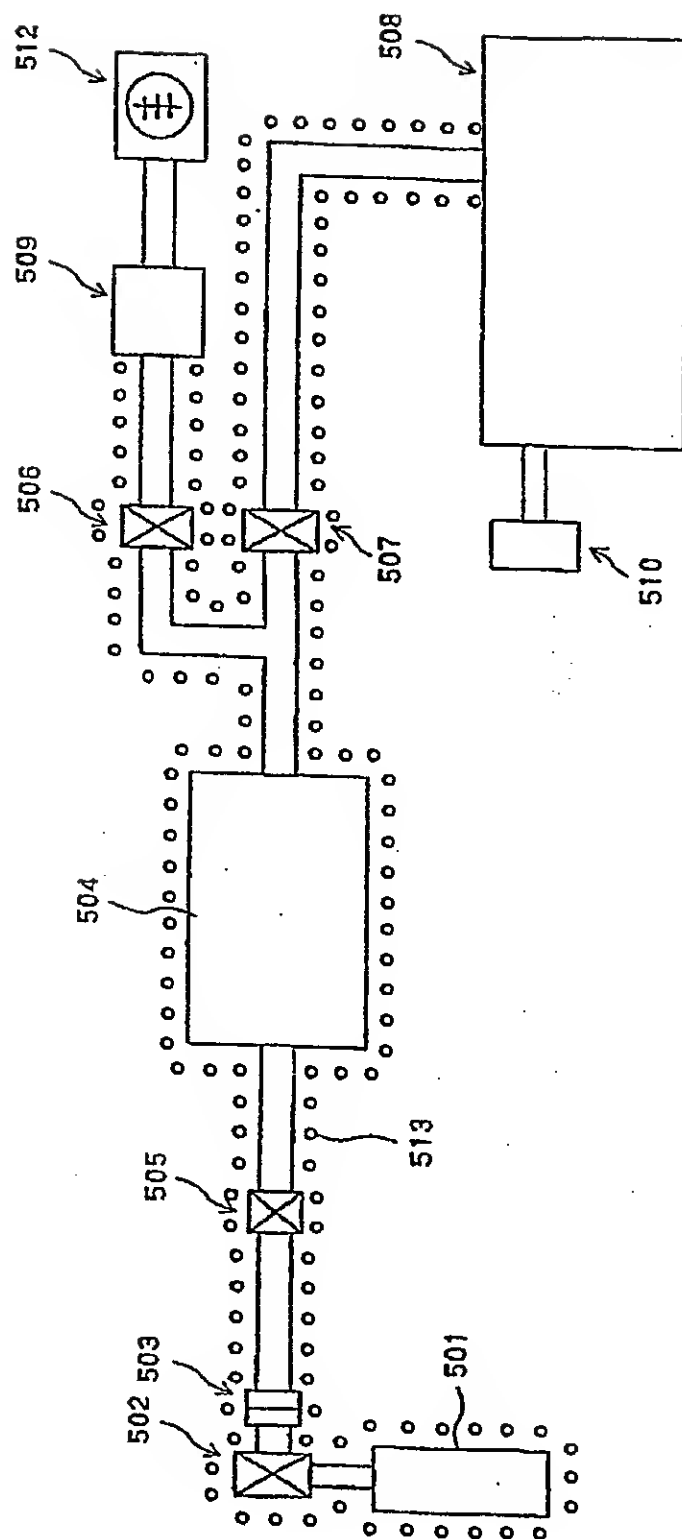
[Fig. 3]



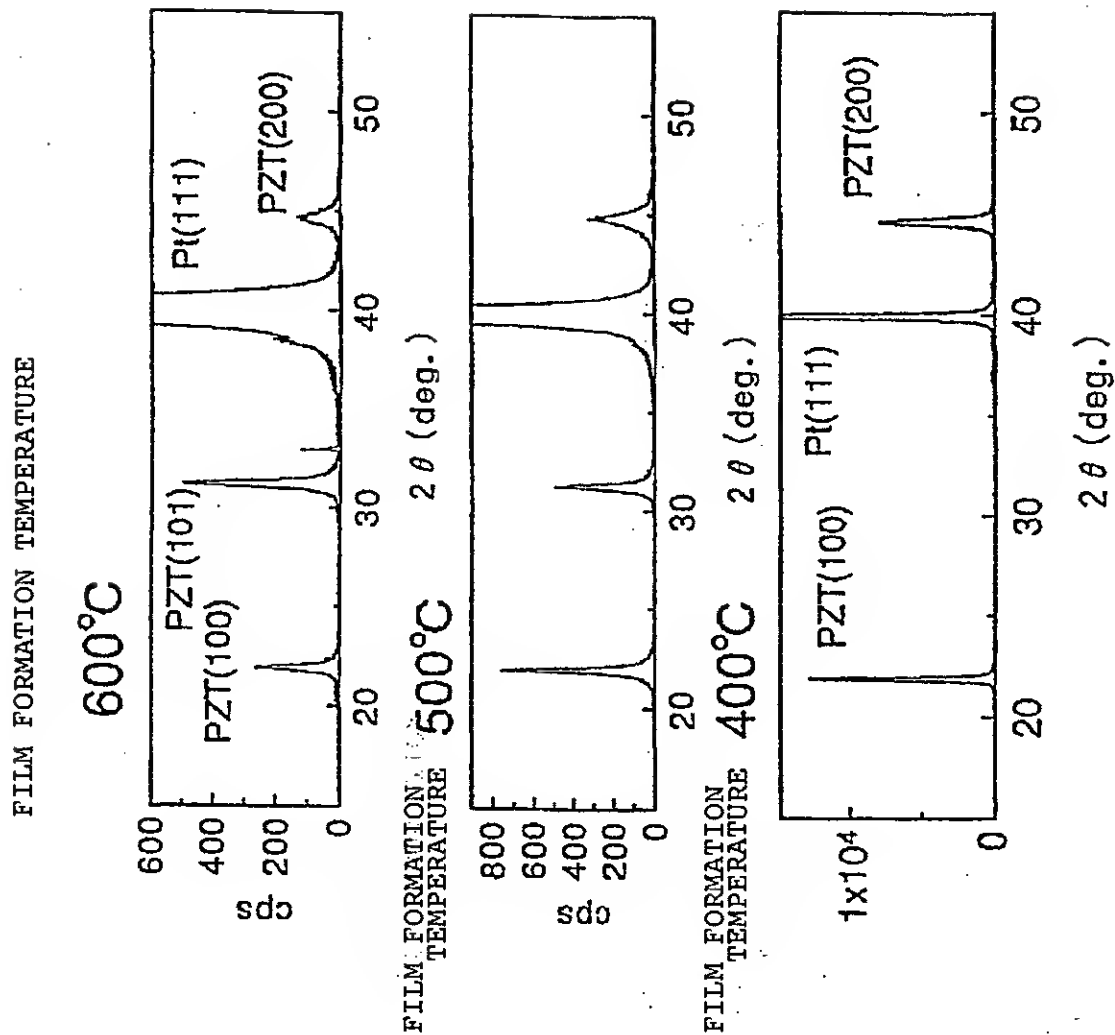
[Fig. 4]



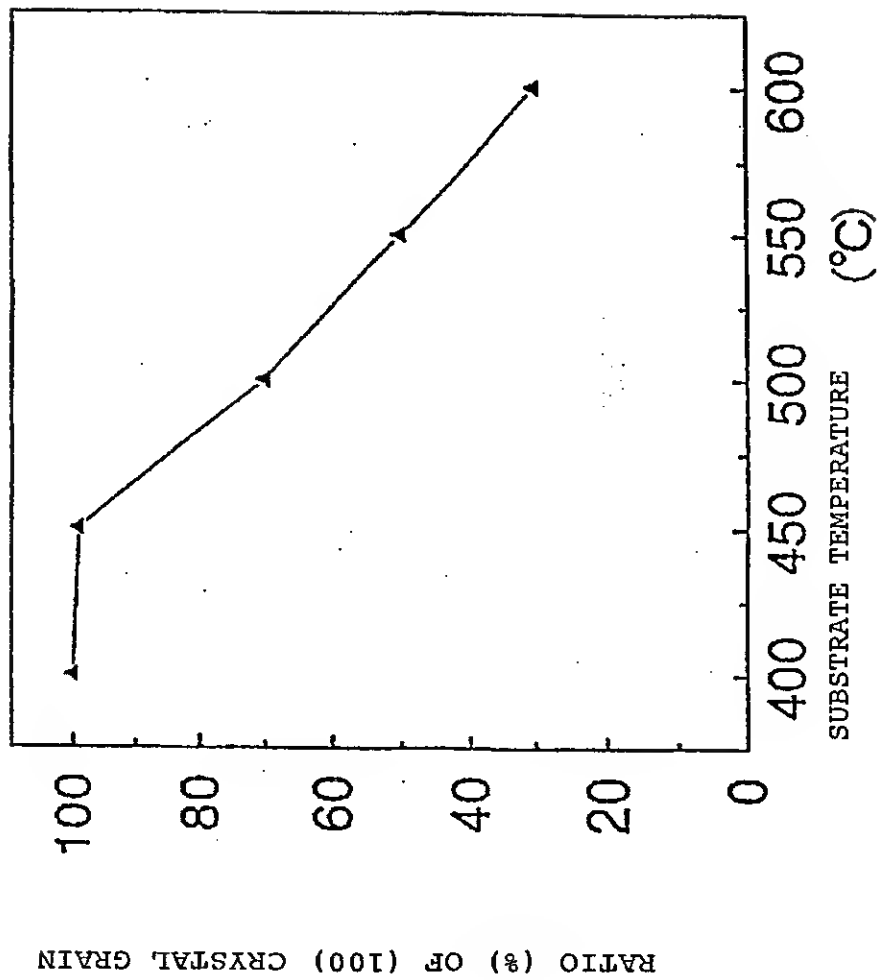
[Fig. 5]



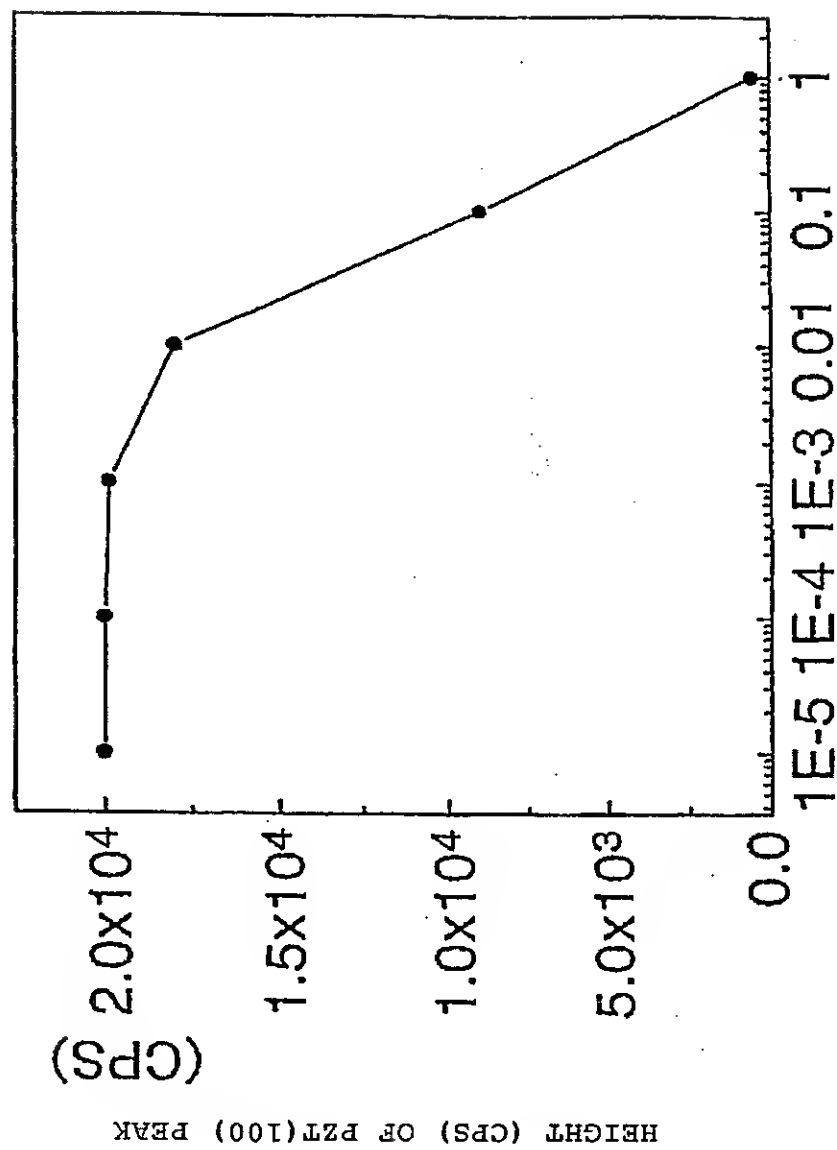
[Fig. 6]



[Fig. 7]

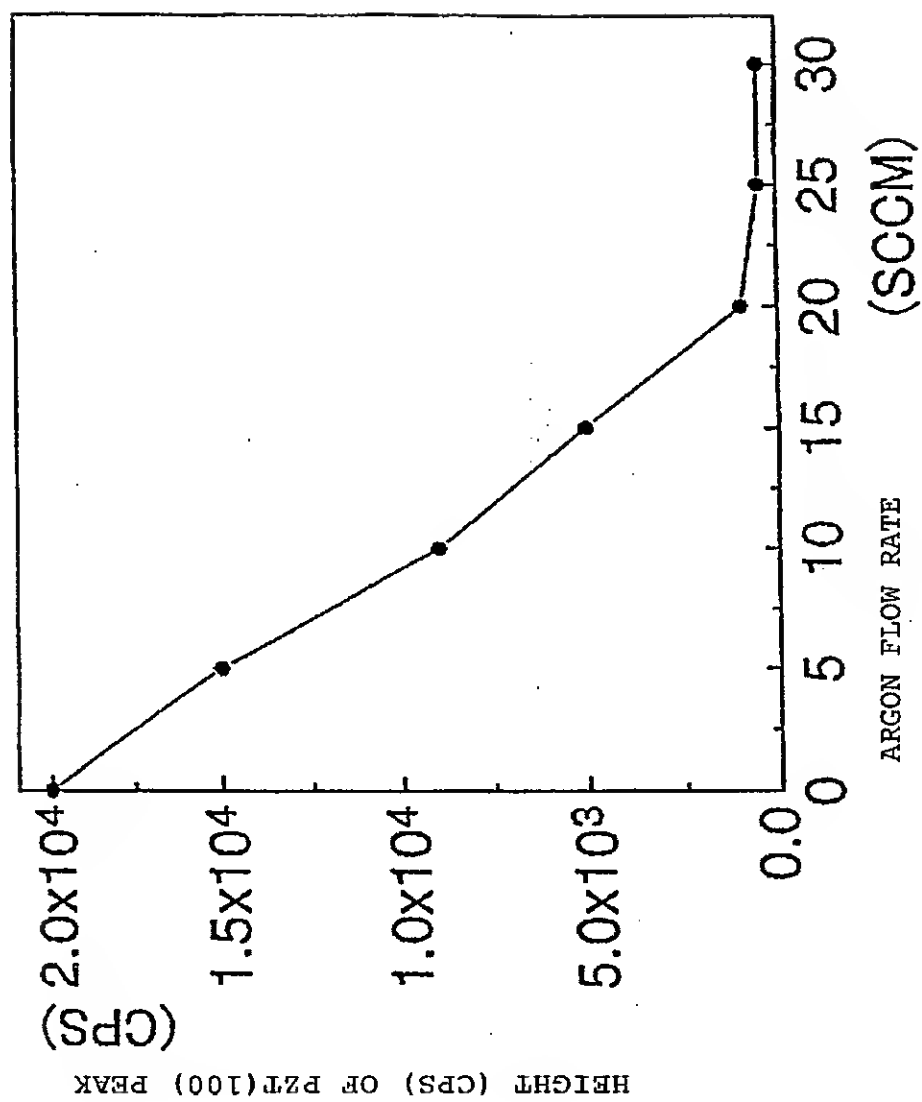


[Fig. 8]

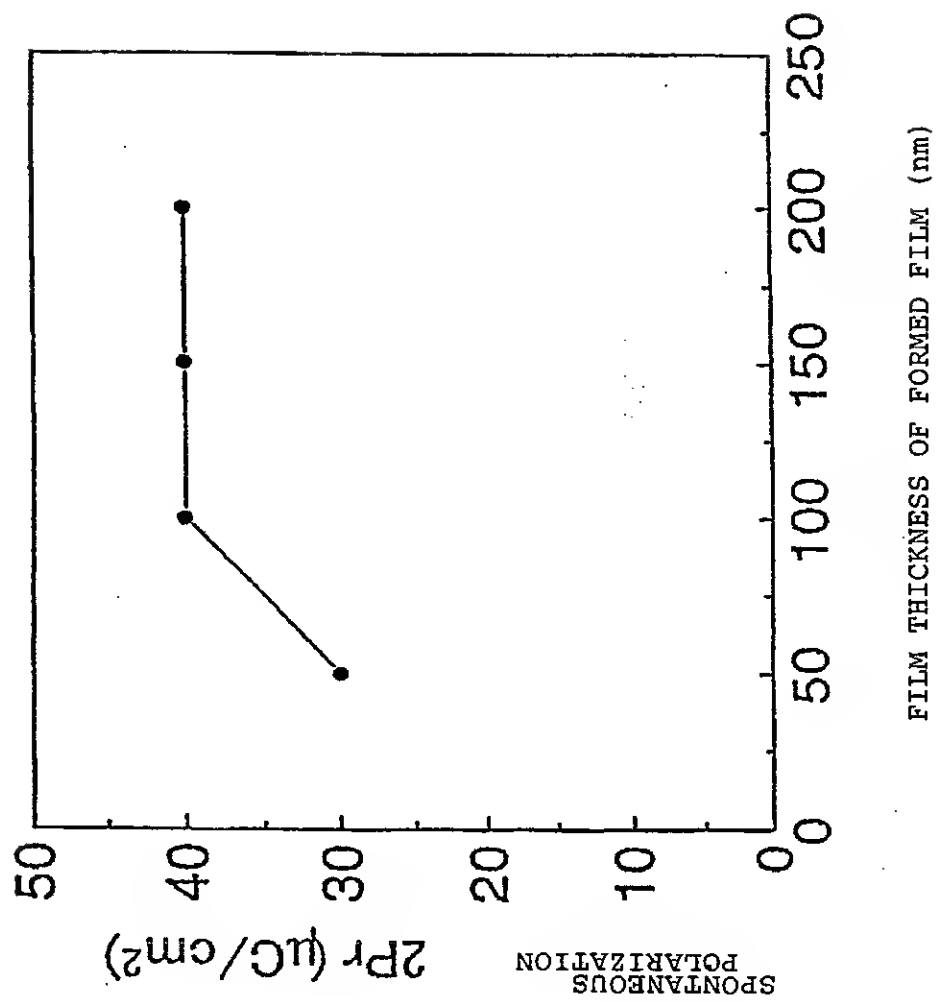




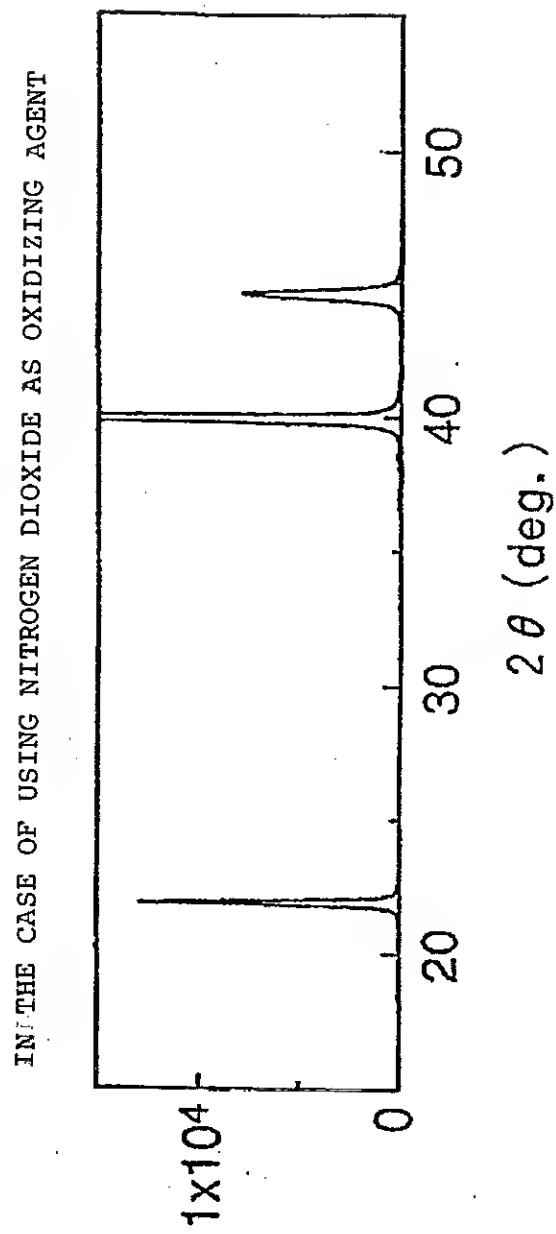
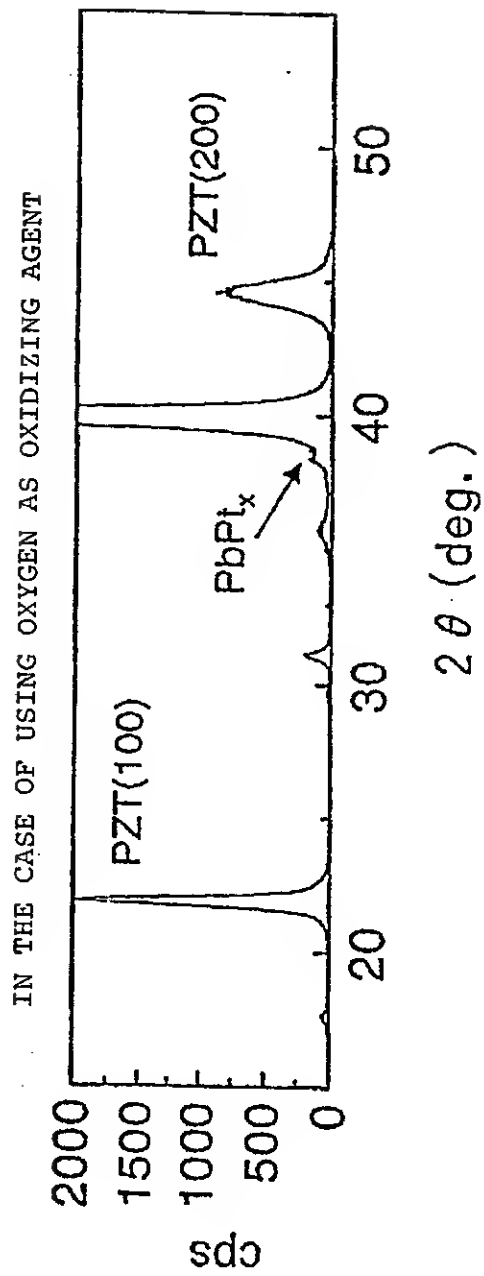
[Fig. 9]



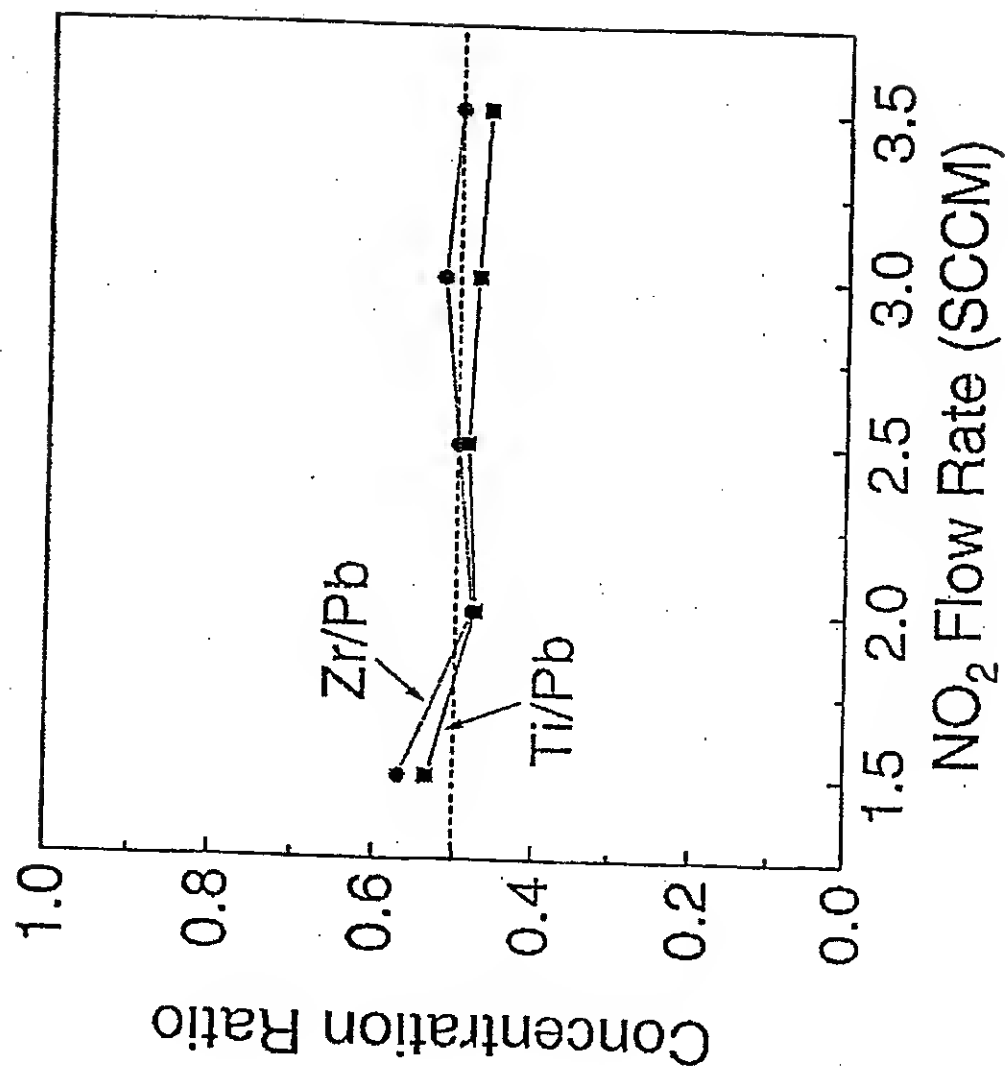
[Fig. 10]



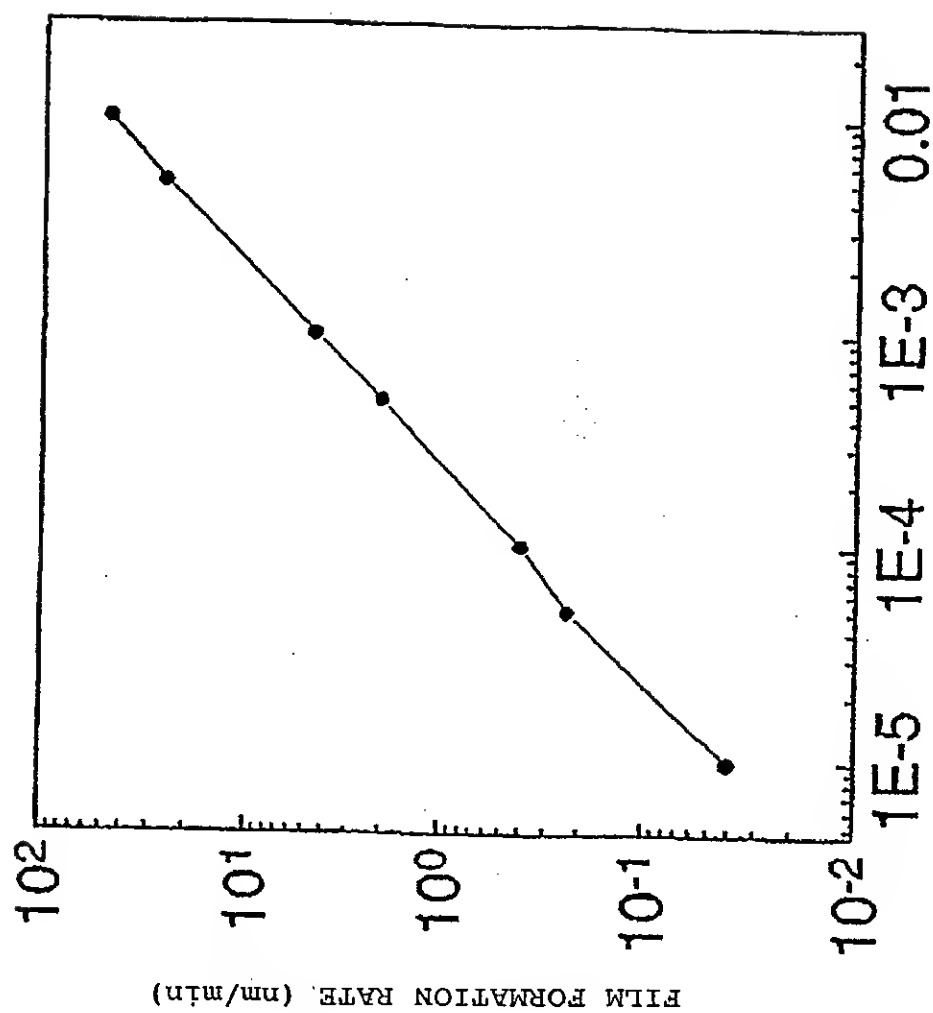
[Fig. 11]



[Fig. 12]

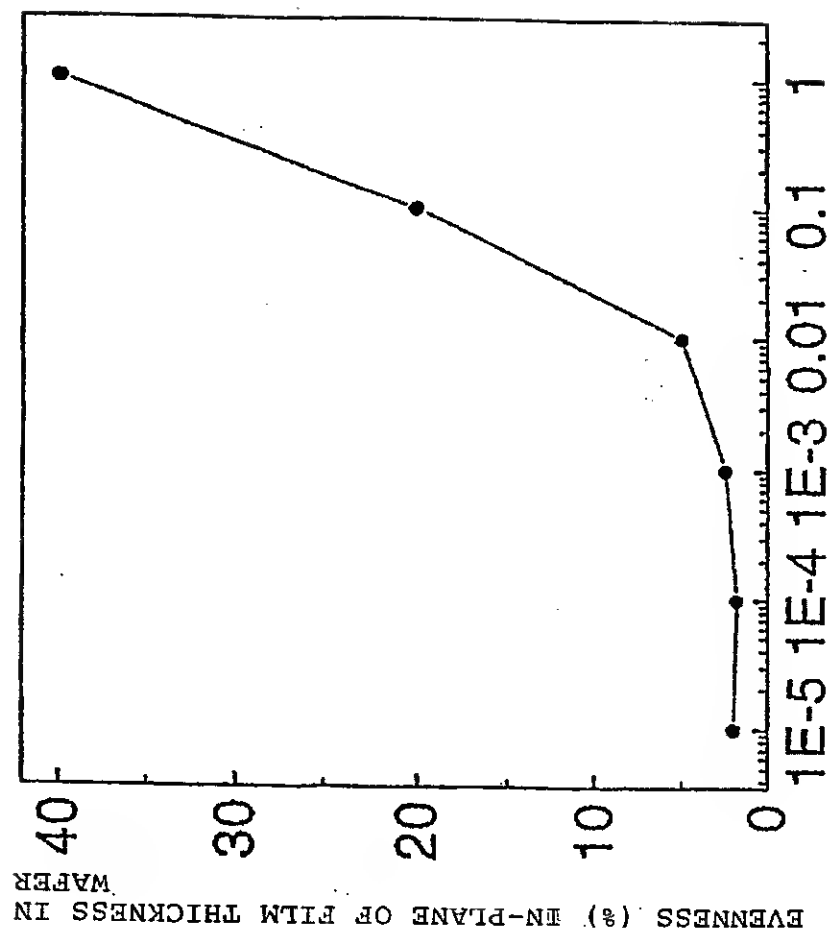


[Fig. 13]

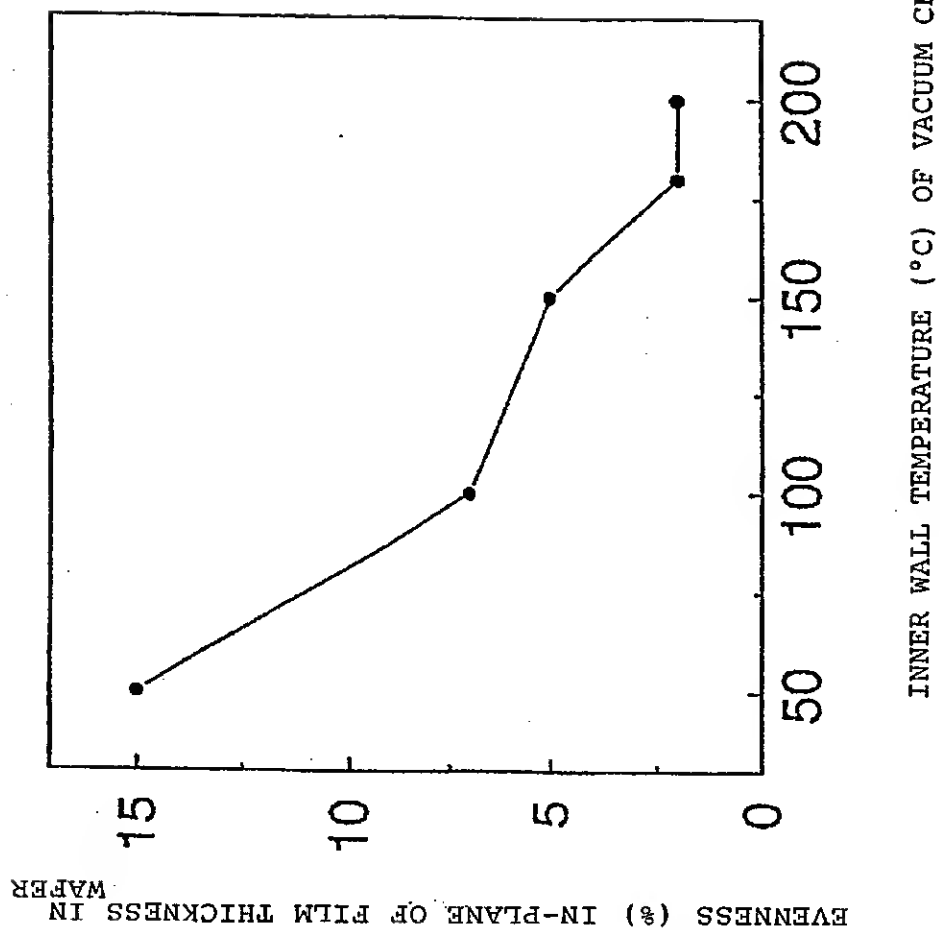


PRESSURE (Torr) AT THE TIME OF FILM FORMATION

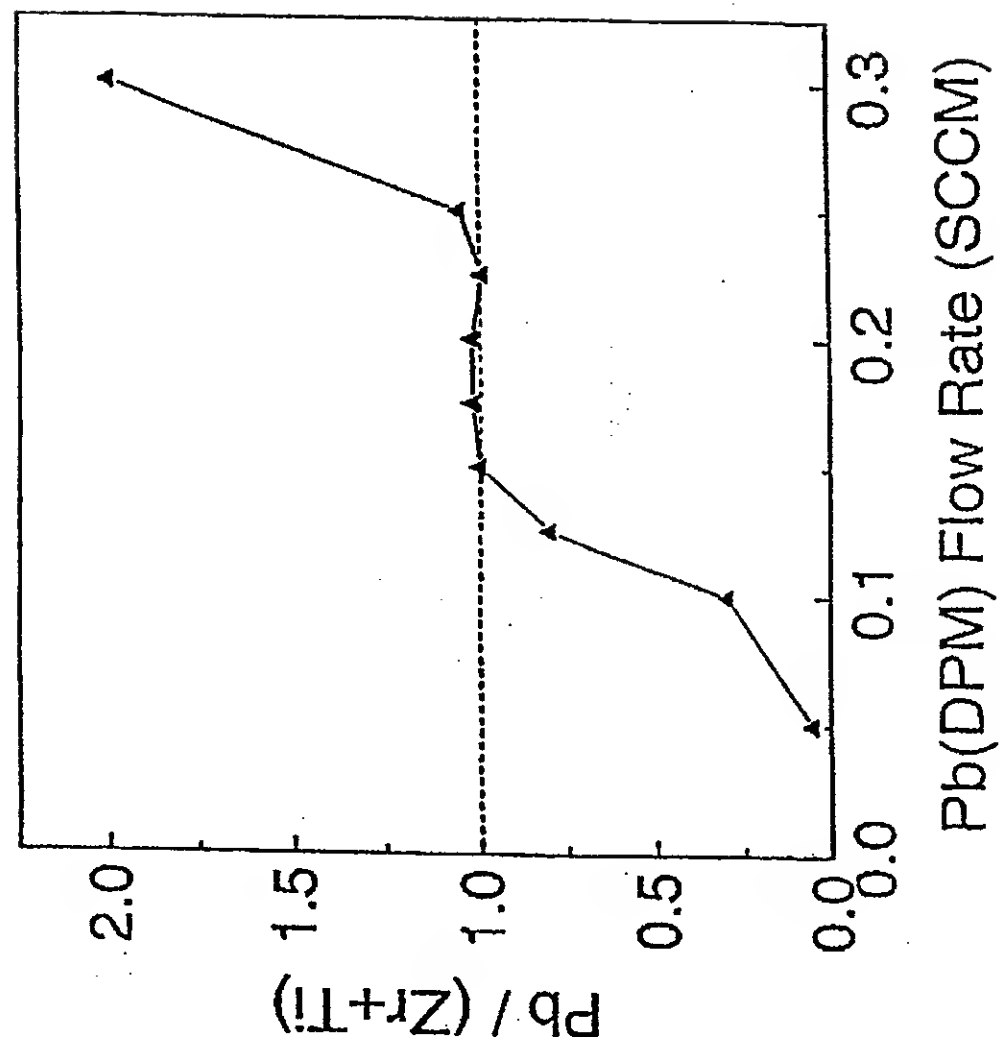
[Fig. 14]



[Fig. 15]

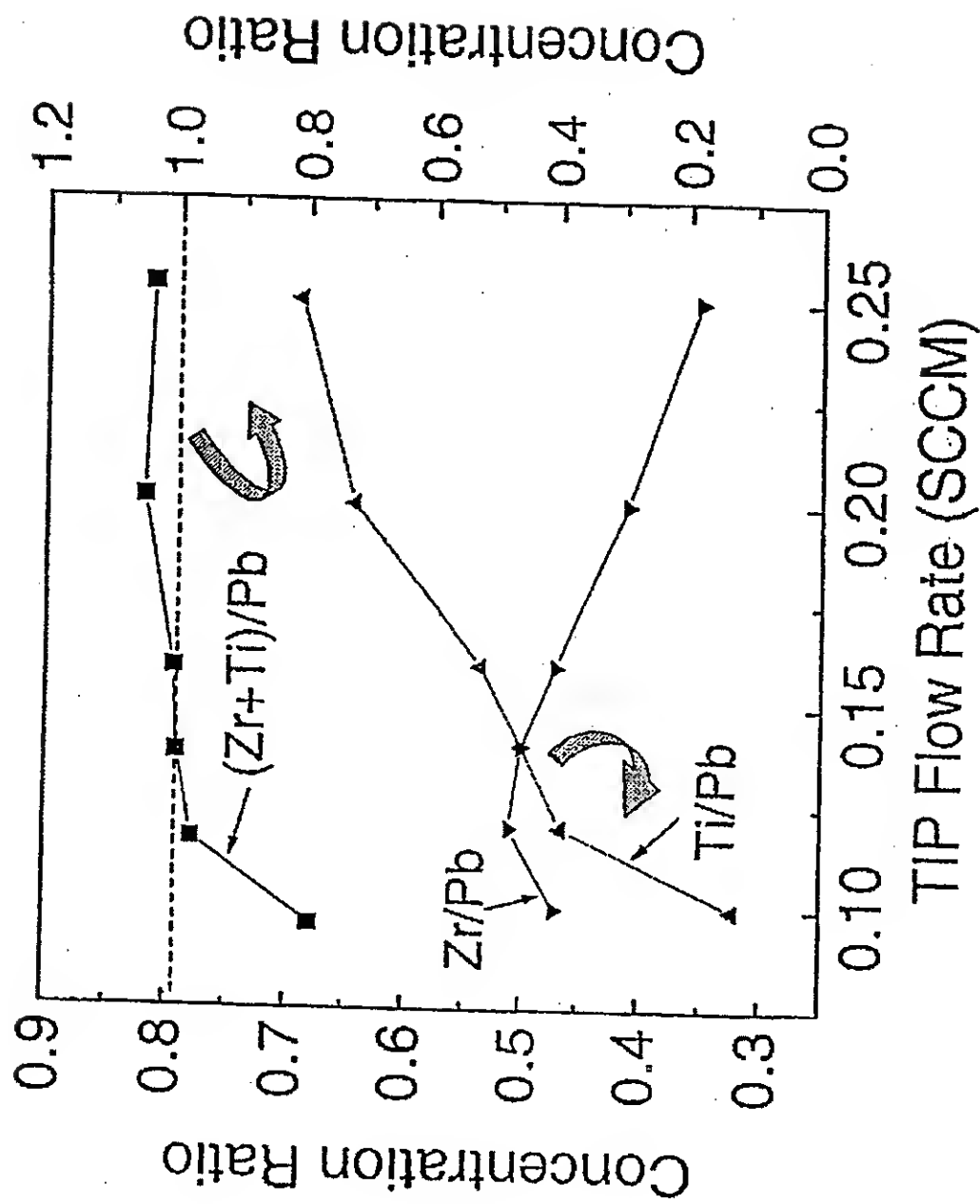


[Fig. 16]



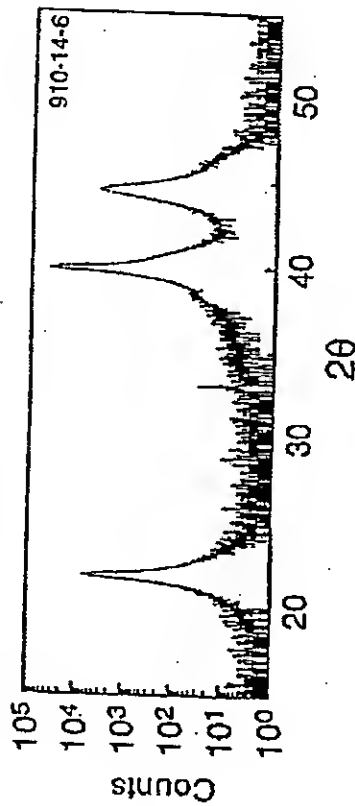


[Fig. 17]

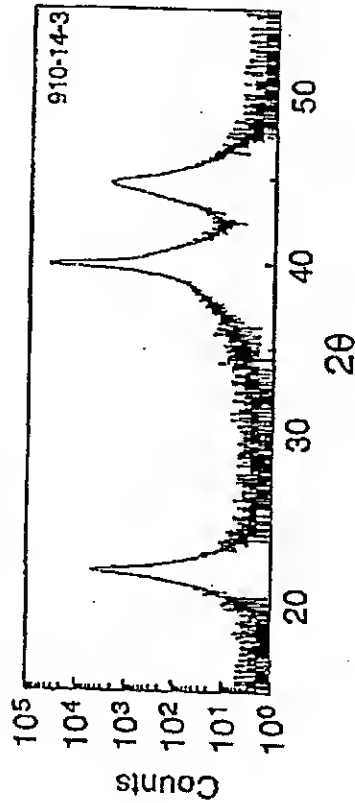


[Fig. 18]

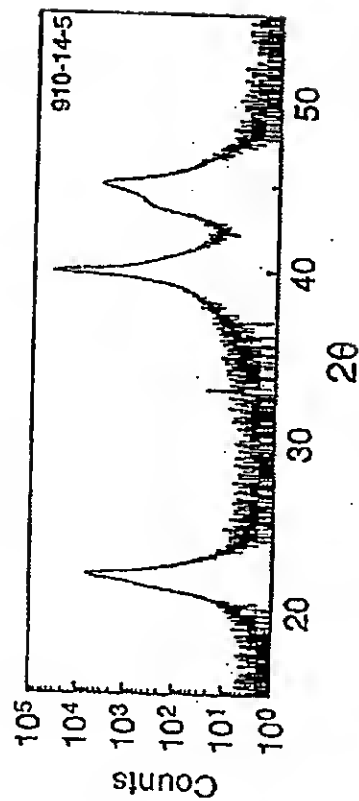
a)  $Ti = 0.16SCCM$



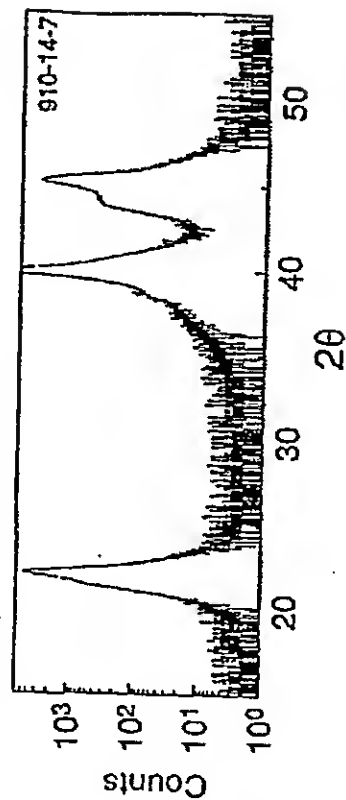
b)  $Ti = 0.18SCCM$



c)  $Ti = 0.20SCCM$

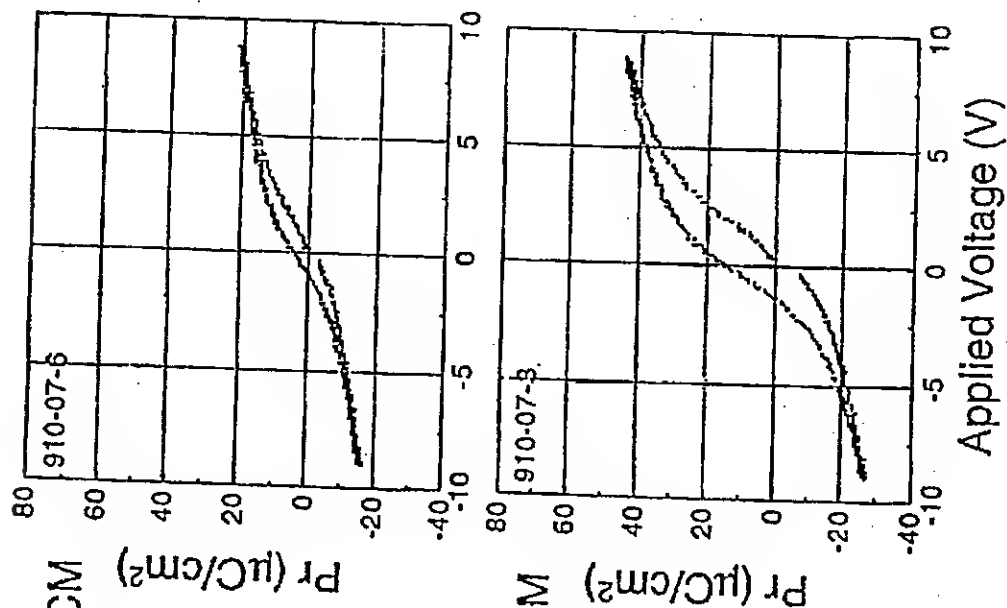


d)  $Ti = 0.22SCCM$

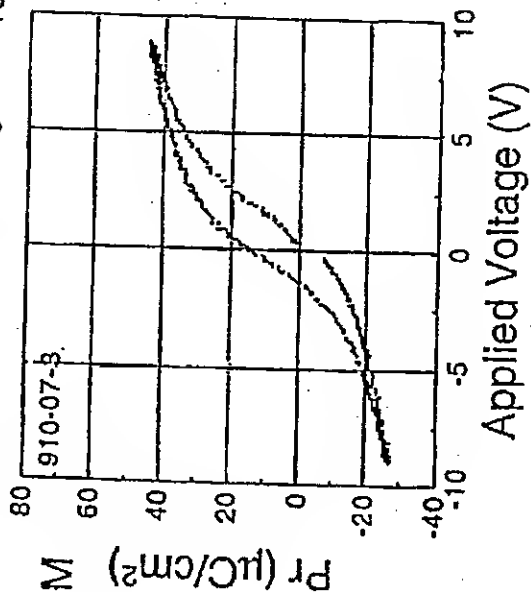


[Fig. 19]

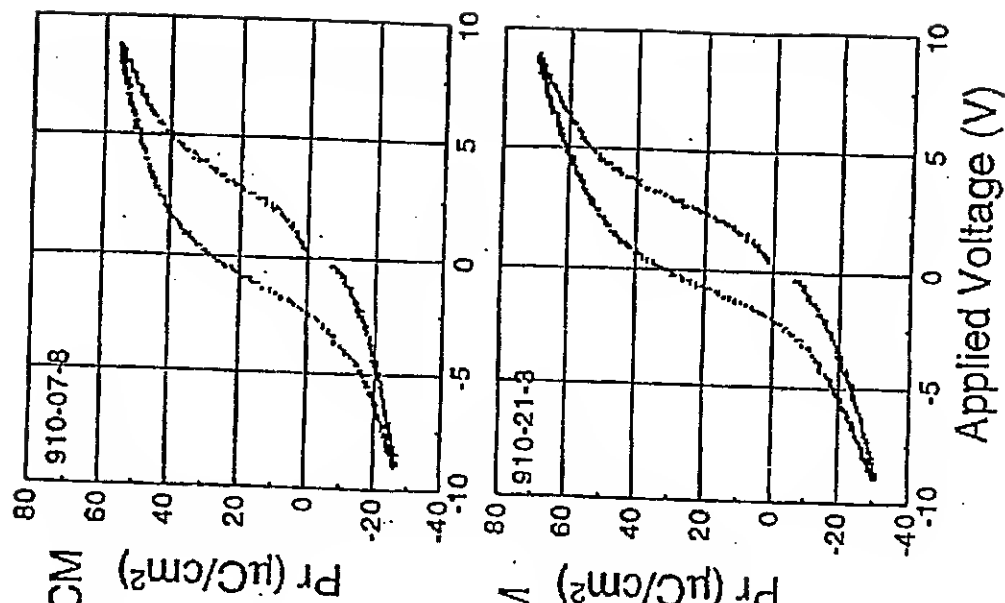
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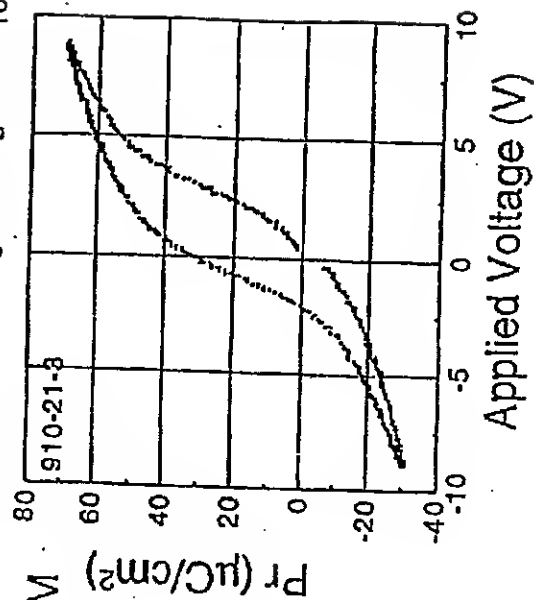
b) Ti =  
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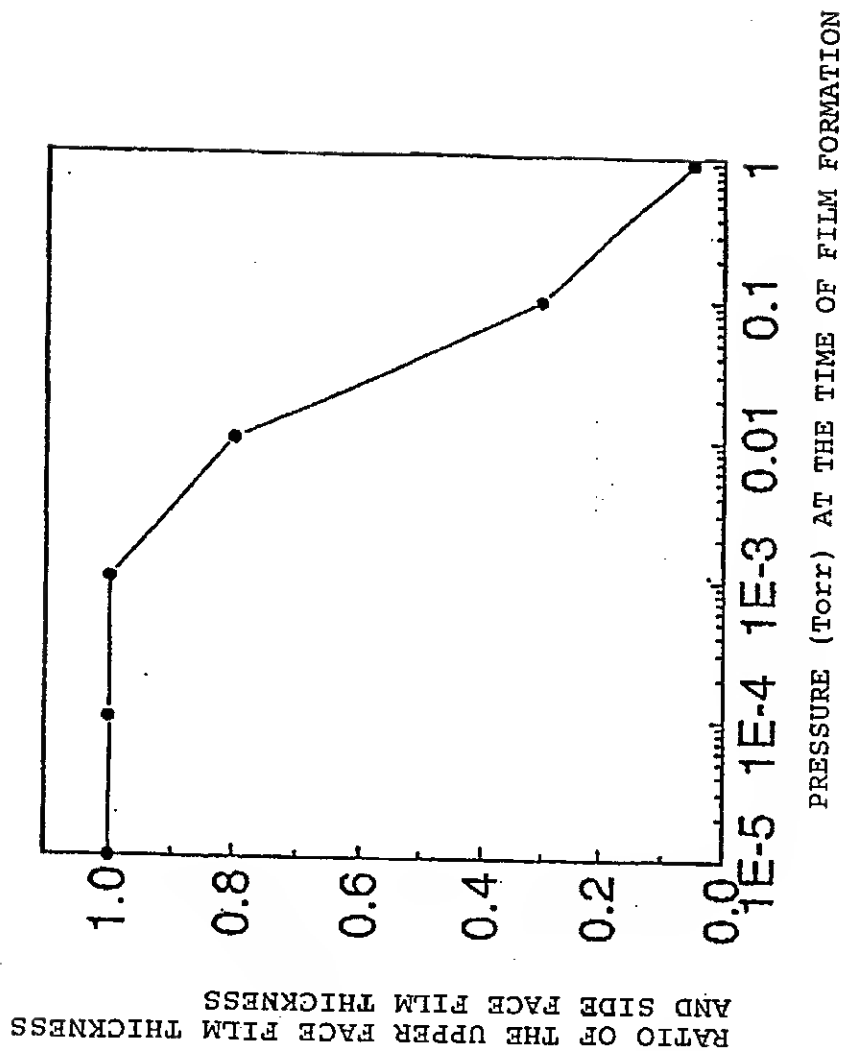
c) Ti =  
0.18SCCM



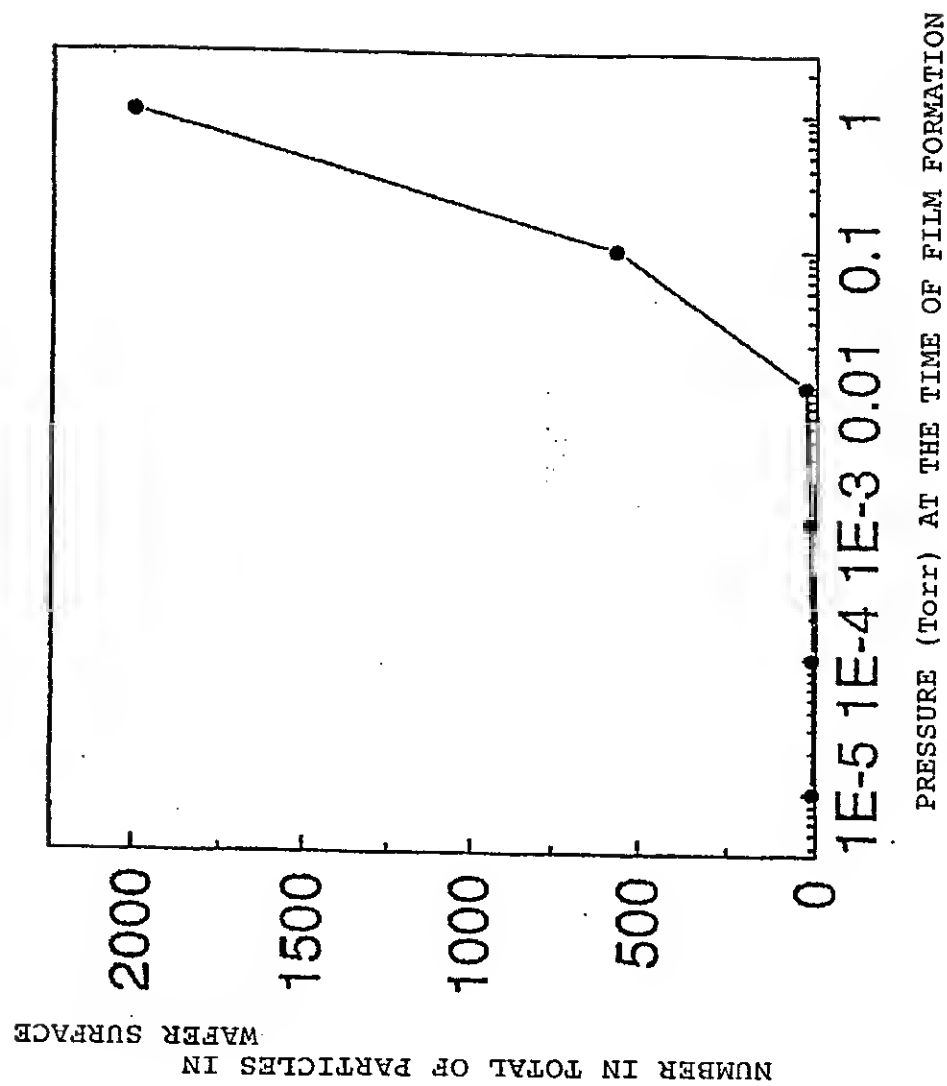
d) Ti =  
0.2SCCM



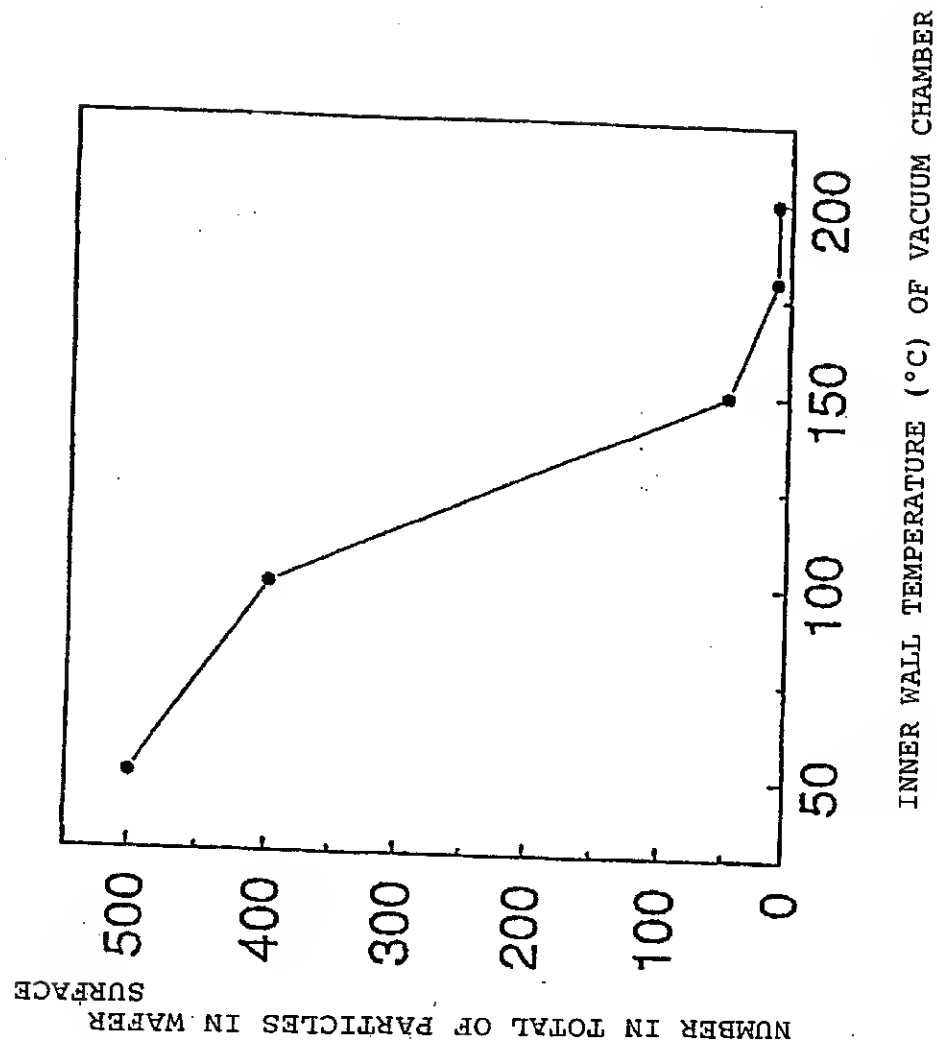
[Fig. 20]



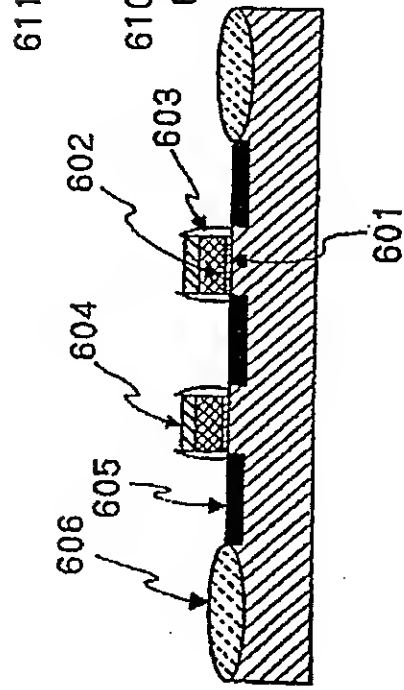
[Fig. 21]



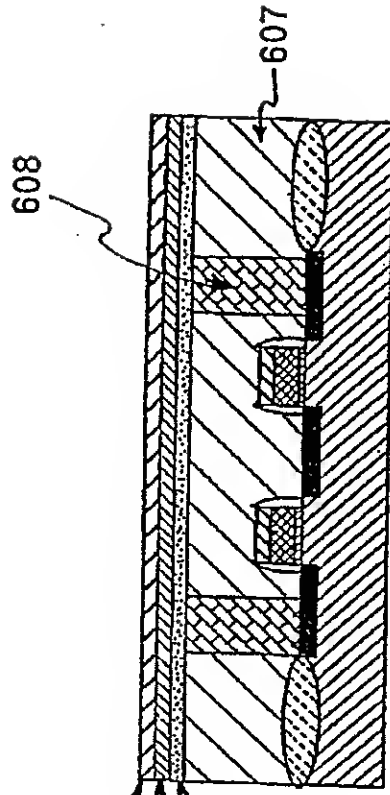
[Fig. 22]



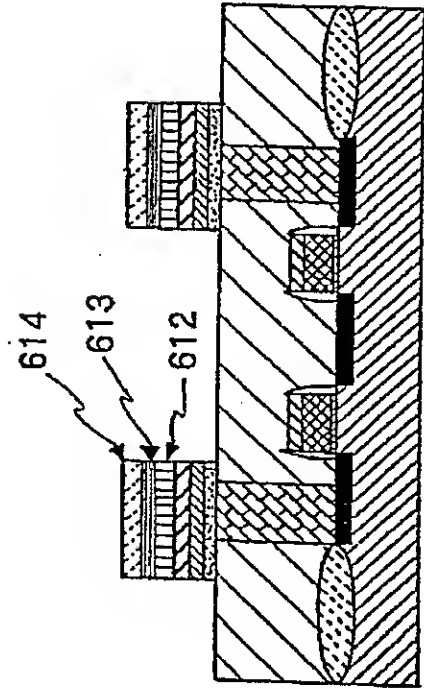
[Fig. 23A]



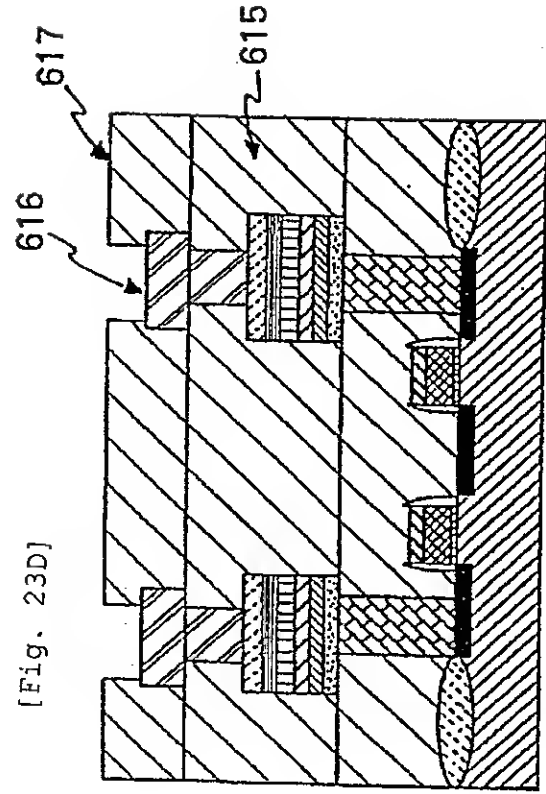
[Fig. 23B]



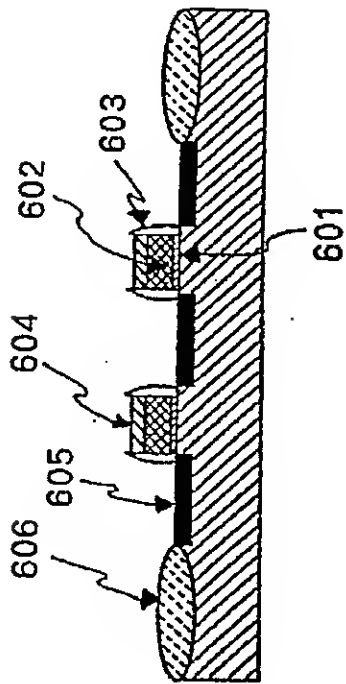
[Fig. 23C]



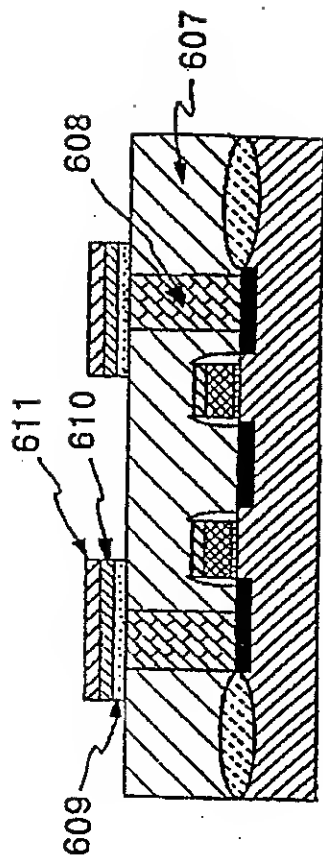
[Fig. 23D]



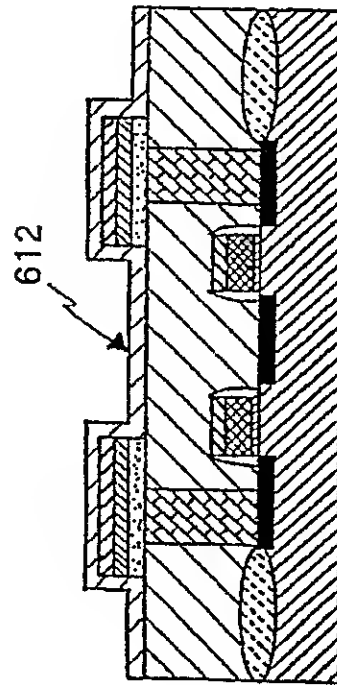
[Fig. 24A]



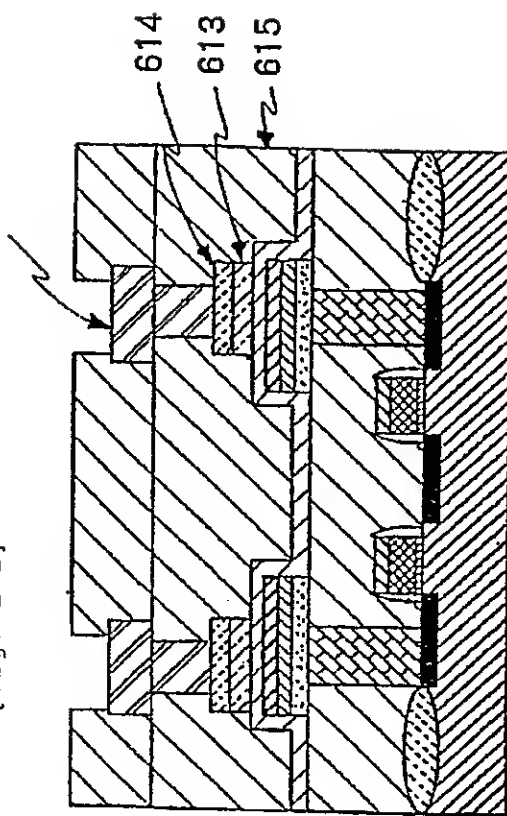
[Fig. 24B]



[Fig. 24C]

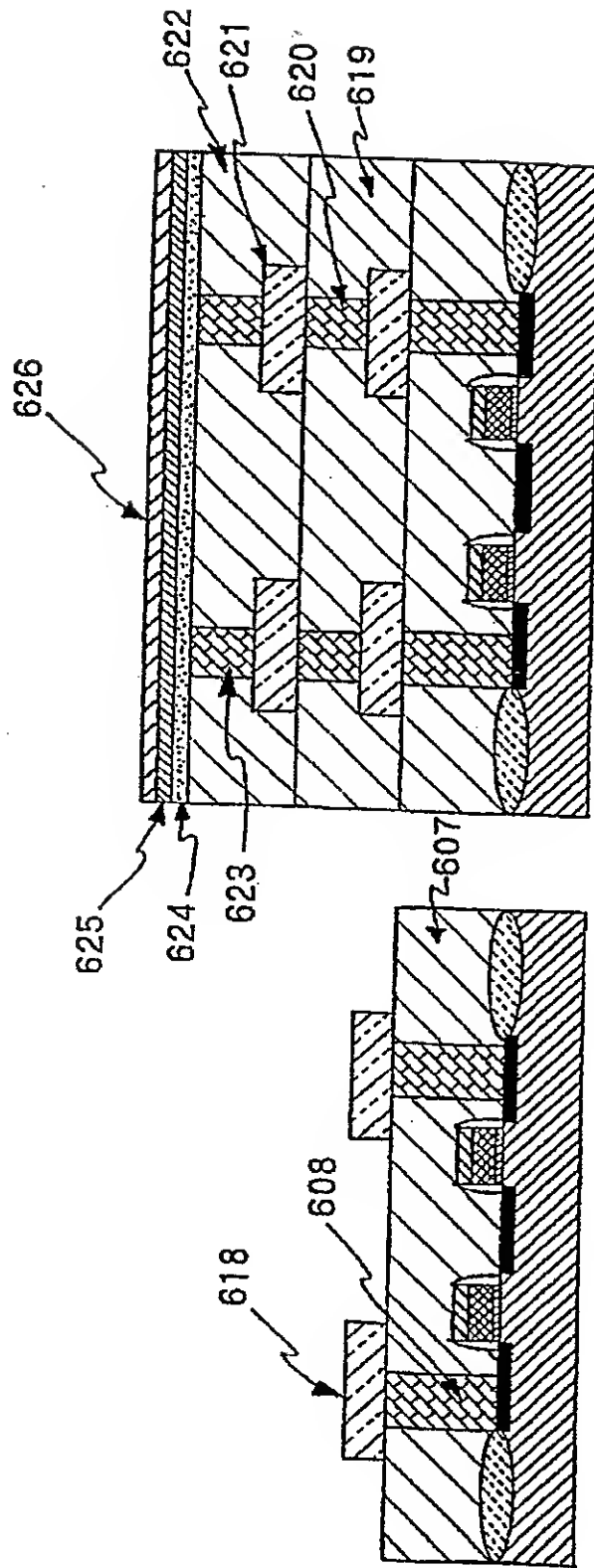


[Fig. 24D]

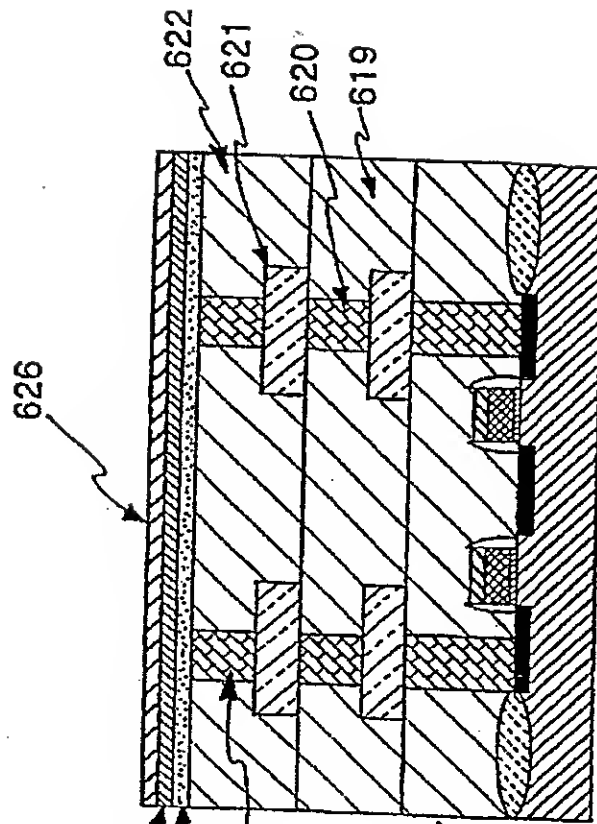




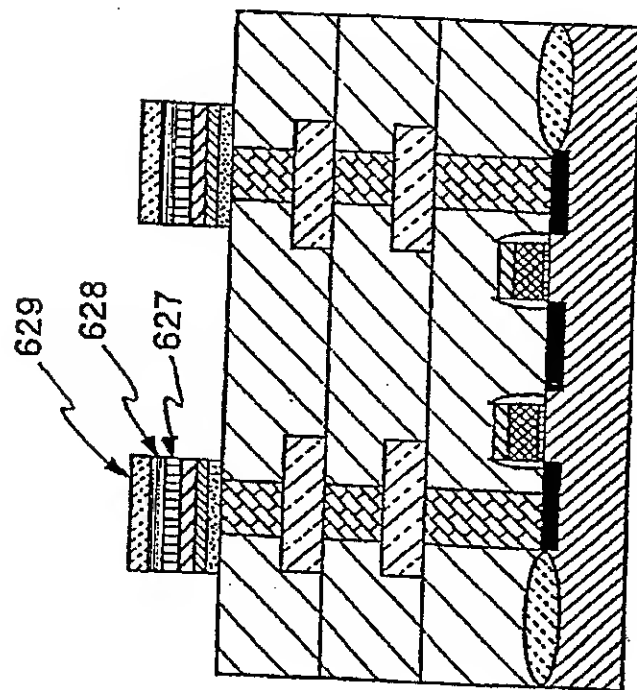
[Fig. 25A]



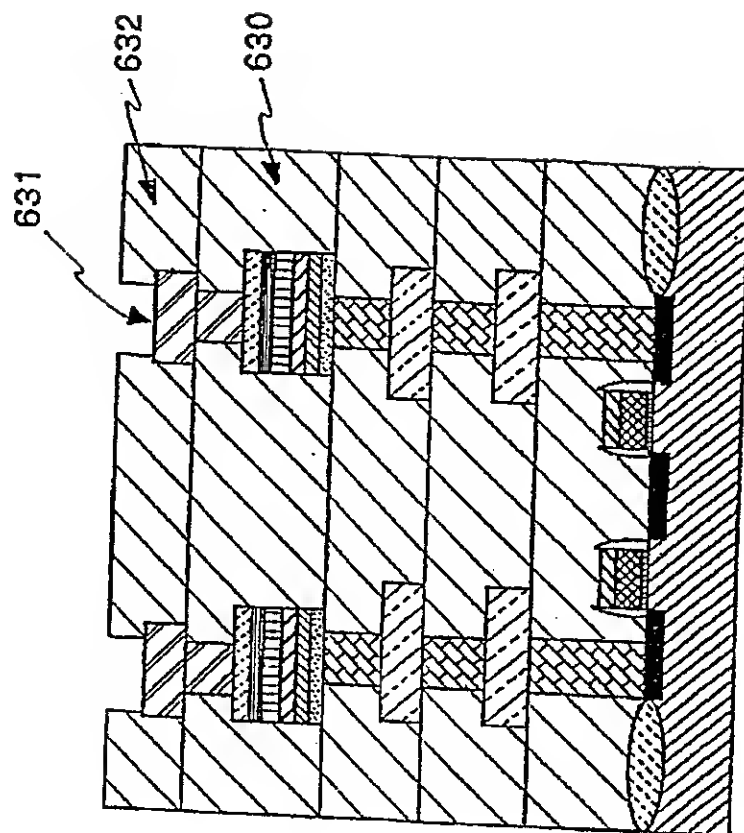
[Fig. 25B]



[Fig. 26C]



[Fig. 26D]



[Document Name]      Abstract

[Abstract]

[Problem] The present invention provides a vapor phase growth method of a metal oxide dielectric film and capable of forming a metal oxide with excellent in both orientation and crystallinity on a plug at a low temperature and further aims at providing a semiconductor device made to have a fine structure, highly integrated, and multilayered and metallized by employing the vapor phase growth method.

[Solution] A vapor phase growth method of a metal oxide dielectric film on a substrate using organometal gases, comprising: a step of carrying out film formation by introducing the organometal gases and an oxidizing gas into a vacuum chamber through separate introduction inlets while heating the substrate set in the vacuum chamber and keeping the total pressure of the vacuum chamber at  $1 \times 10^{-2}$  Torr or lower.

[Selected Drawing] Fig. 1